Ab initio study of interaction between magnetic adatoms on metal surfaces

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We present systematic *ab initio* calculations for the interaction energies of 3*d* adatoms on the Cu(001) surface. The calculations are based on density-functional theory in the local-density approximation and apply the Korringa-Kohn-Rostoker Green's function method. Short-range interactions and oscillatory long-range interactions between magnetic adatoms are calculated. We demonstrate that magnetism has a strong impact on the interaction energies. Total-energy calculations show that the atomic exchange process at the surface between all the 3*d* adatoms and the Cu substrate atoms is energetically favorable even for metals immiscible in bulk.

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I. INTRODUCTION

The knowledge of adatom-adatom and adatom-substrate interactions is of great importance for the understanding of a variety of physical and chemical phenomena on metal surfaces.[1–4] The most obvious ones are diffusion, cluster formation, film growth, surface reactivity, adsorption, and desorption. The recent experiments have shown that the atomic exchange at the interface can lead to different adatom species on the surface. For example, in the case of Co/Cu(001) substitutional Co, on-surface Co, and on-surface Cu atoms were detected in experiments.[5] The energetics effects and the kinetic barriers influence on the structure of the interface. Interactions between on-surface atoms, as well as the interactions between substitutional ones determine the growth modes.

The magnetic properties at the atomic scale are also dictated by the interaction between adatoms.[6,7] Adatom-adatom interactions have several origins:[1,8–10] at small interatomic distances direct electronic interactions dominate; at large separations adsorbate interactions are indirect and mediated by substrate electrons and by deformation of the substrate lattice. In the case of magnetic adatoms direct or indirect exchange coupling between spins of adatoms is involved in the interactions. Direct magnetic coupling between adatoms at a short distance can strongly affect magnetic ground states of small clusters.[11] Indirect exchange interaction is expected to influence on the Kondo effect in magnetic nanostructures.[12] The competition between exchange and bonding interactions can lead to rich magnetic behavior.[6]

Over the past several years experimental methods such as ion field[1,13] and scanning tunneling microscopy (STM)[14] made it possible to monitor the individual atoms directly. Adatom-adatom interactions have been determined by measurements of the pair distributions of diffusing adatoms on metal surfaces.[13,15,16] The most remarkable finding is that a low temperature STM allows one to resolve long-range adsorbate interactions mediated by surface states up to 80 Å.[15,16] These interactions have been predicted in 1978 by Lau and Kohn.[9] *Ab initio* calculations have demonstrated that indirect adsorbate interactions on (111) metal surfaces can significantly influence surface diffusion and the growth morphology.[17,18]

The most recent STM experiments performed with single magnetic adatoms, dimers, and small magnetic clusters[19–22] raise the possibility of a direct study of interactions in magnetic nanostructures at the atomic scale. The ability to probe and manipulate individual magnetic atoms opens up the door for studying artificial atomic-scale magnetic structures. The magnetic and electronic properties of such structures vary dramatically depending on their size and shape.[23]

Both short-range and long-range interactions between magnetic adatoms as well as the interaction between magnetic adatoms and the surface are of fundamental interest. To our knowledge, little attention, if any, has been paid so far to *ab initio* studies of these problems.

It is the goal of this paper to present *ab initio* calculations of the interaction energy between magnetic adatoms on a metal surface. The discussion will be concentrated on the 3*d* magnetic adatoms on Cu(001). Adsorbate interactions of the electronic origin at short and large distances are calculated. We demonstrate that magnetism has a strong impact on the interactions between magnetic adatoms as well as on the interaction of adatoms with the substrate and leads to magnetic energy anomalies. The effect of atomic relaxations on the interaction energy is demonstrated for Co adatoms on the Cu(001). Total energy calculations show that the atomic exchange process at the surface between the 3*d* adatoms and the Cu substrate atoms is energetically favorable even for metals immiscible in bulk.

II. METHOD OF CALCULATION

Our calculations are based on density-functional theory in the local spin density approximation and Korringa-Kohn-Rostoker Green's function method for impurities and clusters on metal surfaces.[7,24] We treat the ideal surface as a two-dimensional perturbation of the bulk. Green's function of the ideal surface and Green's function of adatoms on the surface are calculated using the multiple-scattering theory. Exchange and correlation effects are included using the potential of Vosko *et al.*[25] The full charge density is taken into account by a multipole expansion up to angular momentum of *l*

$=6$. Coulomb and exchange correlation energies are calculated using $l_{max}=12$. Atomic relaxations are determined by calculating the forces acting on adatoms by means of an ionic version of the Hellmann-Feynman theorem[26] in the full potential approximation. Details of the method and its several applications can be found elsewhere.[7,24] The most recent application of our method for calculations of electronic states of Co islands on Cu(111) has shown very good agreement with the experiments.[27]

The interaction energy between the two adatoms on (in) the surface is defined as the total-energy difference between two states: (1) the final state where the two adatoms are located at the nearest-neighbor sites and (2) the initial state where both adatoms are infinitely far away on the surface. To overcome finite-size effects due to the restricted finite extension of the perturbation around adatoms, the total energy of the system is evaluated by applying Lloyd's formula[28] adapted to complex energies. We use the above approach for calculations of interaction energies between adatoms at short distances (up to 6 Å).

At large adsorbate distances the interaction energies are very small (a few milli electron volt), therefore there is the problem of subtracting huge total-energy values to obtain the resulting small interaction energies. The screening of adatoms by the substrate electrons ensures that the main contribution to the interaction energy at large adatom-adatom separations is well approximated by the single-particle energies alone, as was proposed by Hyldgaard and Person.[29] Recent experiments of Knorr *et al.*[16] have revealed an excellent agreement with the theory of Hyldgaard and Person. It is also important to note that the magnetic interaction between monolayers at large distances is well described by the single-particles energies alone.[30] Our calculations for the interaction energies between $3d$ adatoms on the Cu surface have shown that even for a small adatom-adatom separations (4–6 Å) the single-particle contribution alone reproduces well the interaction energies. For example, for the adatom-adatom distance 5.7 Å the interaction energy between the two Co adatoms calculated using only the single-particle energies is 10 meV, which is very close to the value 12.9 meV obtained in the total-energy calculations. Therefore, we are convinced that using of the single-particles energies for calculations in a surface environment at large adsorbate separations is well justified.[31]

In the present work we employ the frozen potential approximation[30] and use the self-consistent potential of the single adatom for the two interacting adatoms at large distances. The single-particle energies are calculated using Lloyd's formula. As a benefit of the frozen potential approximation, calculations can be performed up to very large distances. However, for distances between adatoms up to 6 Å we perform the self-consistent total-energy calculations to determine the interaction energy.

III. SHORT-RANGE ELECTRONIC INTERACTION BETWEEN MAGNETIC ADATOMS

In this section we discuss the electronic interaction between magnetic adatoms at the nearest-neighbor sites on the Cu(001). We have performed self-consistent calculations of the total energy and magnetic moments of the $3d$ dimers on the Cu (001) surface for ferromagnetic (FM), antiferromagnetic (AFM), and nonmagnetic (NM) configurations. We have to note that the density-functional theory always allows one to find the NM state performing non-spin-polarized calculations. In Fig. 1 we present the total-energy difference between the FM (AFM) state and the NM one for all $3d$ pairs. Our results reveal that a NM configuration is an unstable state for all $3d$ pairs. In other words, magnetic solutions (FM or AFM) are lowest in energy. We find that around the center of the transition metal series (V, Cr, and Mn) AFM states are the most stable ones for $3d$ dimers. For Ti and Ni dimers we did not find stable AFM solutions. The total energy of the AFM state for Mn dimer is only 4 meV lower than the FM one. It is useful to recall our investigations of Mn clusters on Ag and Cu surfaces.[11] We have shown that supported Mn clusters exhibit magnetic bistability. Sessoli *et al.*[32] reported the observation of magnetic bistability of ligated Mn metal ion clusters.

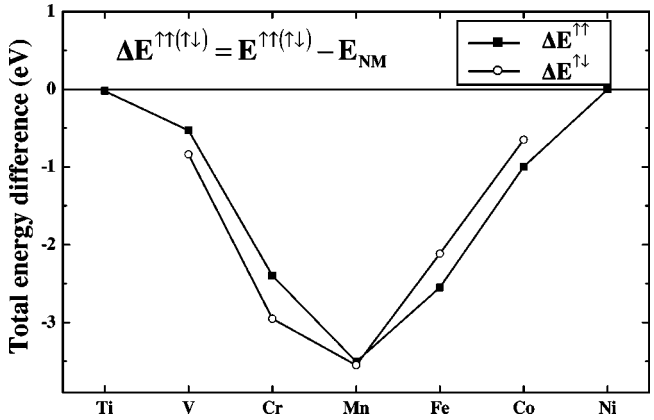

FIG. 1. (a) Total-energy difference between ferromagnetic (antiferromagnetic) and nonmagnetic states for $3d$ pairs; for Ti and Ni pairs only ferromagnetic and nonmagnetic solutions exist. Solid squares refer to the ferromagnetic pairs; open circles refer to the antiferromagnetic pairs.

The magnetic moments of $3d$ dimers for the lowest energy states and the isolated adatoms are presented in Fig. 2. We have to note that the magnetic moments for ferromagnetic and antiferromagnetic states are very close. The largest local moments are obtained for Cr and Mn. Because of the more extended nature of the d orbitals at the beginning of the $3d$ series magnetic moment for Ti is considerably reduced compared to the moment of the isolated adatom. In the case of the Fe and Co dimers the changes of the moments are very small, because the $3d$ wave functions of these elements are well localized and the majority bands are practically filled. While we obtain that the Ni adatom is nonmagnetic, the Ni dimer has a small magnetic moment. It has been found that at the end of the series the d-d interaction can enhance the moments in clusters and monolayers compared to a single adatoms.[33]

Figure 3 shows the calculated interaction energies between $3d$ adatoms at the nearest-neighbor sites on Cu(001) for different magnetic configurations. Negative energies

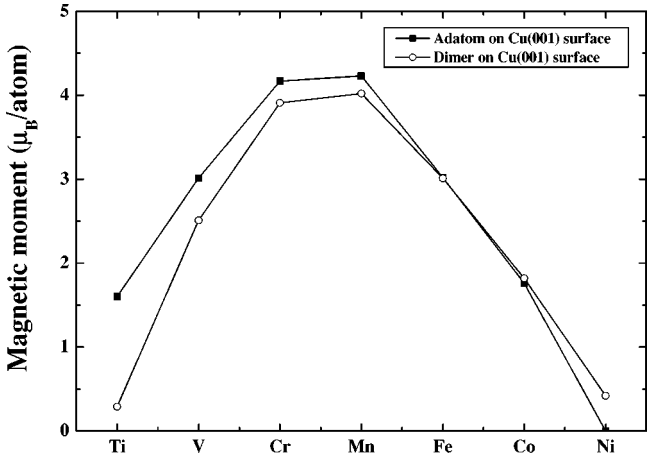

FIG. 2. Local magnetic moments of 3*d* adatoms and dimers on Cu(001). The ground-state solutions are presented. The magnetic moments per atom are given in Bohr magnetons.

mean attraction between adatoms. We find that magnetism has a strong impact on the interaction energies. Magnetic energy anomalies are well seen in the middle of the series: a paramagnetic calculation gives a parabolic curve, whereas a spin-polarized calculation results in a double-peak structure. Thus, interaction energies of the magnetic dimers in the middle of the series are strongly reduced compared to the nonmagnetic ones. A similar anomaly also occurs for the surface and cohesive energies of the 3*d* metals for the solution energies of 3*d* impurities in noble metals and for their binding to vacancies.[34] Recently, it has also been shown that magnetism reduces segregation energies of magnetic materials embedded in nonmagnetic hosts.[35] One can see in Fig. 3, that the interactions in the V and the Cr dimers in ferromagnetic configurations are weaker than in the antiferromagnetic ones, but for the Fe and the Co dimers the interaction in the ferromagnetic state is stronger than in the antiferromagnetic one. These results are a consequence of frustrations: the two V or Cr adatoms would like to couple antiparallel to each other and to form the antiferromagnetic configurations, while for the Fe and the Co pairs the ferromagnetic state is the

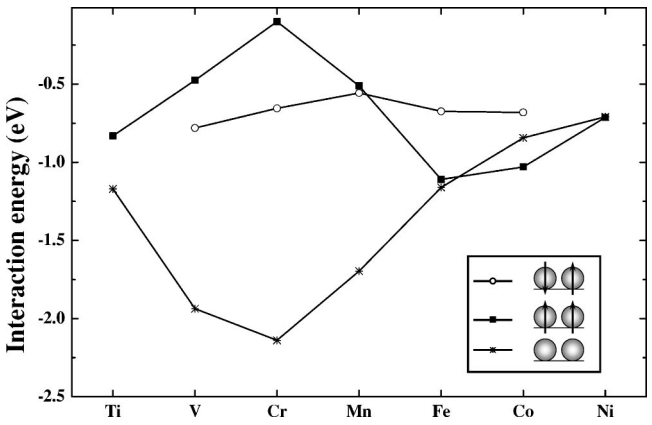

FIG. 3. Interaction energies between two 3*d* adatoms on Cu(001) for the nearest-neighbor sites. Interaction between nonmagnetic, ferromagnetic, and antiferromagnetic pairs are presented.

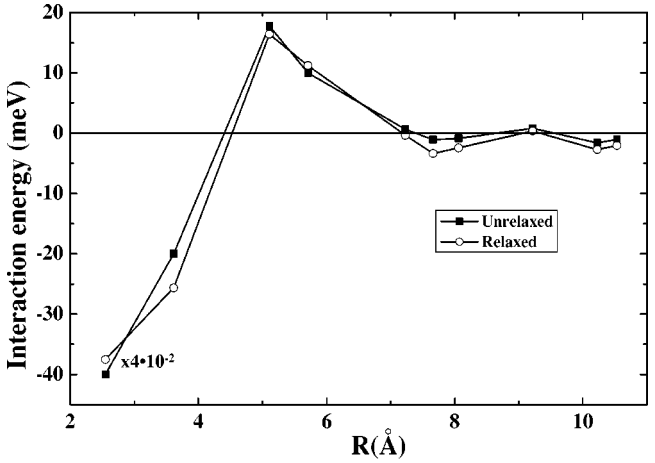

FIG. 4. Long-range interaction between Co adatoms on Cu(001). Calculations for unrelaxed and relaxed geometries are shown. Relaxed vertical positions of adatoms above the surface were determined calculating the HF forces, see the text. For the Co atoms at the nearest-neighbor sites the bond length was also optimized.

ground one. At the same time (cf. Fig. 3), there is nearly no difference between the interaction energy for the Mn pairs in the ferromagnetic and the antiferromagnetic configurations.

The effect of magnetism on the adatom-adatom interactions can be understood considering the change of the magnetic moment due to pairing of the two adatoms. In the tight-binding approximation[36] the change of the interaction energy due to the change of the magnetic moment is defined as $\Delta E_{mag} = -(J/2)[(M+\Delta M)^2 - M^2]$, where ΔM is a change of the magnetic moment due to pairing of the two adatoms. Results for magnetic adatoms and dimers discussed above show that for all dimers, except for Co and Ni dimers, ΔM has the negative value for both FM and AFM states. Thus, the magnetic part of the interaction acts repulsively for the Ti, V, Cr, and Mn pairs. For Co the magnetic moment in the dimer configuration is slightly larger than for the single adatom and as the result, the magnetic interaction increases the interaction energy. For the Fe adatom the magnetic moment is well saturated and magnetic part of the interaction is very weak. The magnetic moment of the Ni dimer is small and therefore the magnetic effects do not affect the interaction energy. It is known that the magnetic contribution to the total energy is determined by the spin-dependent exchange correlation energy alone.[34] Therefore, an increased tendency for magnetism for isolated adatoms compared to dimers, results in a gain of exchange energy and leads to magnetic anomalies in the interaction energies for adatoms with large magnetic moments.

IV. LONG-RANGE INTERACTION BETWEEN ADATOMS

Now our discussion will be concerned with adatoms at longer distances where the interaction between them is expected to be indirect, mediated by the substrate electrons. As an example, we perform calculations for the energy of interaction between the Co adatoms up to a distance of 10 Å.

Our results presented in Fig. 4 show that the interaction

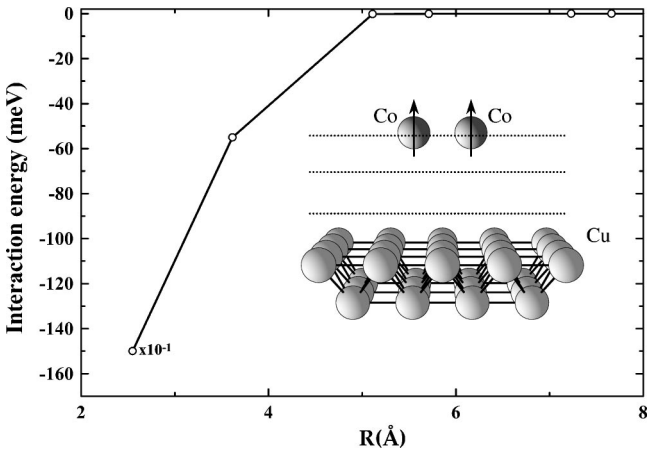

FIG. 5. Interaction between Co adatoms confined to the positions to three layers above the surface.

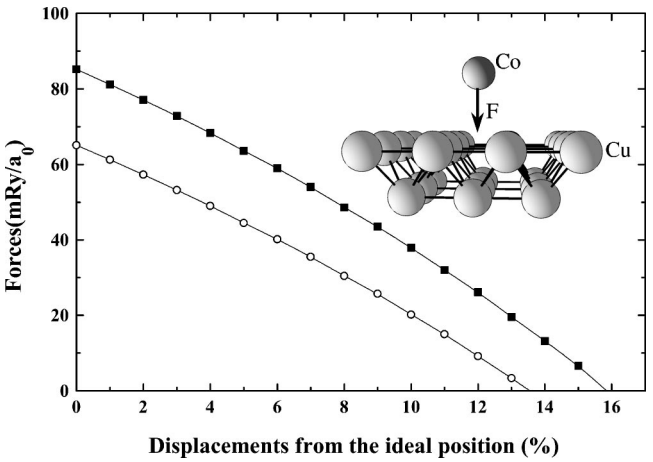

FIG. 6. Forces acting on Co adatom near Cu(001). Open circles refer to magnetic Co adatom, solid squares refer to calculations without spin polarization.

energy is clearly oscillatory. There is a repulsion towards dimer formation for the interatomic separation between 4 and 6 Å. Lau and Kohn predicted such oscillatory interaction in the asymptotic region of large adsorbate separations to decay as $1/r^5$.[9] However, for the distances probed in our calculations the asymptotic behavior is not reached yet.[37]

To demonstrate that the oscillatory form of the interaction is caused by the substrate electrons, we calculate the interaction for the Co atoms confined to the positions to three layers above the surface (5.4 Å), where the interaction between adatoms and the surface is strongly reduced. The results obtained are presented in Fig. 5 and show that in this case the interaction is only attractive and very short range. We expect that the repulsive interaction between 5 and 6 Å can influence on the Co growth on Cu(001) in the early stages of the heteroepitaxy and can lead to a self-assembly of one-dimensional similar structures recently found by Kohn and Ehrlich.[38] Atomic scale simulations are currently underway to assess the growth of Co islands on Cu(001) with long-range interactions between adatoms.

Now we turn to the discussion of the effect of atomic relaxations on interaction energies. Here we present our results for Co adatoms on Cu(001). First, we calculate the Hellman-Feynman forces acting on the adatom near the surface. We have found that in a fully relaxed geometry the distance of the Co adatom from the surface is reduced by 14% compared to the ideal layer distance of Cu(001) (Fig. 6). Relaxation of Cu surface atoms due to the interaction with the Co adatom is very small, less than 2% for the topmost surface layer. In the relaxed geometry the moment of the Co adatoms is reduced by 7%. We have found that the vertical relaxation of the Co dimer is smaller than for the Co adatom. Our results reveal that the dimer approaches surface by about 7% and the bond length is reduced by 4% in the relaxed geometry. For the nearest-neighbor position the interaction energy is increased by 0.1 eV in relaxed geometry compared to the ideal position. The interaction between Co adatoms in the relaxed geometry is shown in Fig. 4. One can see that the substrate-mediated interaction is essentially unmodified by the inclusion of the relaxation.[39] A similar result has been found by Fichthorm and Scheffler,[18] and Bogicevic *et al.*[17]

V. SURFACE ALLOYING ON THE ATOMIC SCALE

Recently several theoretical and experimental studies have reported that the interfacial intermixing can occur even for metals immiscible in bulk form.[40–43] For example, it was found that Co, Fe, and Ni atoms intermix with Cu atoms on the Cu(001) surface.[42] In the case of Co/Cu(001) atomic exchange processes lead to a bimodal initial growth of Co/Cu(001).[5] One of the most striking features of an interface mixing in Co/Cu(001) has been recently discovered. It was found that Co particles burrow into the Cu(001) substrate.[44] Simple arguments to understand the atomic intermixing are based on such macroscopic properties as surface and interface energies and they are rather questionable when applied to an individual adatoms. Therefore, in order to get a deeper insight into the atomic exchange at the interface we perform *ab initio* calculations of the difference in the total energy for exchange process as it is shown in Fig. 7. We find that all $3d$ magnetic adatoms lower the energy of the system

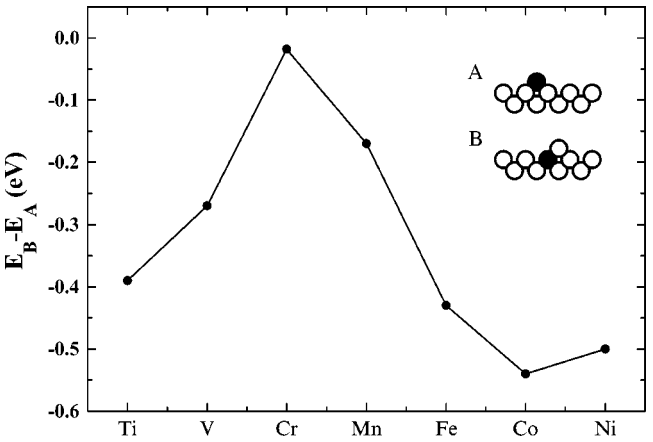

FIG. 7. Energetics of the exchange process. Energy difference between complex *B* and *A* is presented.

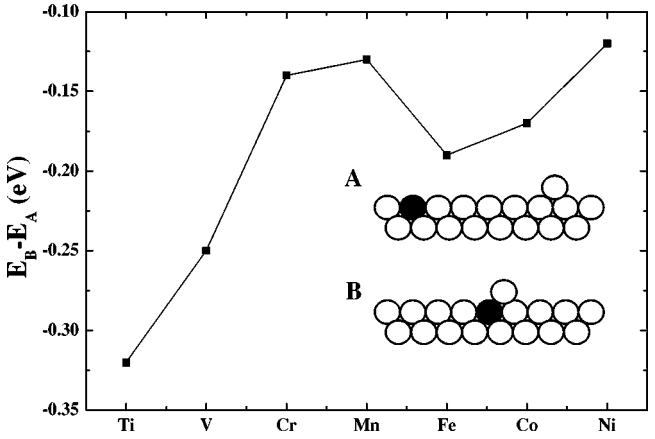

FIG. 8. The direct and the complete exchange processes. Energy difference between complex *B* and *A* is presented.

when they lie inside the Cu(001) substrate, more than when they are adsorbed on the top of it. The energy gain is particularly large for the Ni, Co, and Fe adatoms.

For the exchange process, it is also important to know the energy when the impurity is in the substrate and the Cu adatom has moved away, i.e., is the interaction energy between the impurity and the Cu adatom attractive or repulsive? We have found that for all 3*d* impurities this energy is attractive, i.e., embedded 3*d* impurities and the Cu atom form a stable pairs (cf. Fig. 8).

Our calculations show that the magnetic moments of 3*d* impurities are reduced in the surface compared to the adatoms (cf. Figs. 2 and 9). In other words, the magnetic system loses magnetic energy in the surface. As the result, the binding between the 3*d* adatoms embedded in the Cu(001) surface should also be reduced. Our calculations for the interaction energies of the 3*d* impurities on the nearest-neighbor sites are presented in Fig. 10. The attractive interaction can promote the segregation, the repulsive one can lead to a solid solution. Results shown in Fig. 10 allow one to conclude that all 3*d* adatoms, except Mn and Ni, attract each other and can

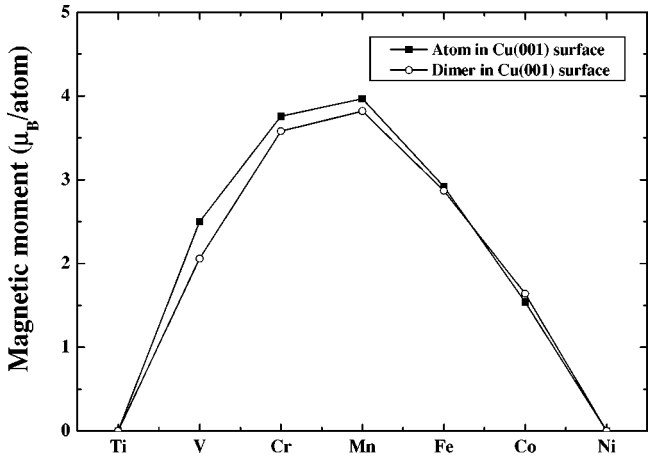

FIG. 9. Local magnetic moments of 3*d* adatoms and dimers in the topmost layer of Cu(001) surface. The ground-state solutions are presented for dimers. The magnetic moments per atom are given in Bohr magnetons.

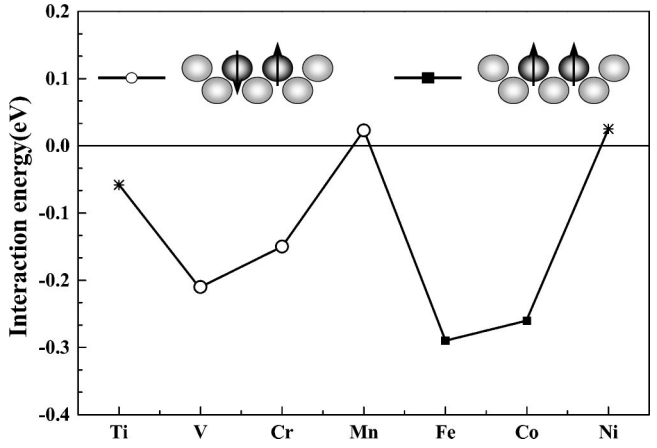

FIG. 10. Interaction energies of 3*d* impurities on the nearest-neighbor sites in the topmost Cu layer. The ground-state solutions are presented. Ti and Ni dimers are nonmagnetic in the Cu surface.

form clusters in top layer on the Cu(001) substrate. Indeed, formation of Co and Fe clusters in Cu(001) was observed experimentally using STM.[42] The Mn and the Ni impurities show repulsion, but the repulsion is weak and not significantly different from zero. We expect that kinetic effects can be crucial to understand surface morphology of Cu(001) with the Mn and the Ni atoms.

Finally, we comment on the influence of magnetism on the energetics of the atomic exchange. As an example, we perform calculations for nonmagnetic Co adatoms on the Cu(001) surface (Gedanken experiment). We find that for nonmagnetic Co adatoms the gain of energy due to intermixing is 1 eV, i.e., considerably larger than for the magnetic adatom (0.54 eV, cf. Fig. 7). Thus, magnetism tends to stabilize 3*d* adatoms on the surface and prevents site exchange. Similar effects were found for magnetic monolayers.[45]

Calculations of the HF forces for magnetic and nonmagnetic Co adatoms at different distances from the Cu(001) substrate are shown in Fig. 6. The behavior of nonmagnetic adatoms on metal surface is determined by increasing their coordination to gain maximum cohesive energy. On the other hand, for magnetic adatoms, a competition between a rearrangement such as to obtain large coordination number and an arrangement with a small coordination number to gain maximum magnetic energy (to decrease the hybridization with the nonmagnetic substrate) takes place. In the case of the nonmagnetic calculations, the forces acting on the Co adatom are larger than forces acting on the magnetic one for any position of the adatom above the surface. This result is essentially unmodified by the inclusion of the relaxation of the substrate atoms. In a fully relaxed geometry (the force acting on the adatom is zero, cf. Fig. 6) the nonmagnetic Co adatom approaches closer to the surface than the magnetic one. This effect can promote the exchange process.

VI. CONCLUSION

We have performed *ab initio* studies for the interaction energies between magnetic adatoms on the Cu(001) surface. It has been shown that the magnetic contribution to the

adatom-adatom binding leads to an anomalous behavior in the middle of the 3*d* series. We have demonstrated that the interaction between the 3*d* adatoms mediated by the Cu substrate electrons is oscillatory. We have found that this interaction at large distances is essentially unmodified by the inclusion of the relaxation of adatoms and the substrate atoms. Our results predict that all 3*d* magnetic adatoms on Cu(001) prefer the surface position to the adatom one and, except Mn and Ni, should form clusters in the surface layers.

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