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Magnetism on Cu(001) due to a Single Transition-Metal Impurity

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Our first principles calculation has shown that single 3d transition-metal atoms embedded in the surface layer of Cu(001) can have considerable magnetic moments. In addition, the Cu atoms closest to the impurity in the same layer also possess appreciable moment, which is not realized if the impurity is embedded in bulk Cu. The calculation indicates that intense d-d interaction and heavy charge exchange between the impurity and the host atoms occur in the surface layer, which therefore facilitates the enhancement of magnetism.

KEYWORDS: magnetic moment, surface impurity, 3d transition metals

§1. Introduction

Most 3d transition metals are associated with magnetism. Recent technological advances take great interests in magnetic thin films, particularly those comprised of 3d transition metals such as Cr, Mn, Fe, Co, and Ni. Thin films or multilayers can be grown in a variety of ways. However, the growth inevitably begins with the deposit of individual atoms. The use of atom magnetism is a natural tendency following the trend of the miniaturization of electronic devices. This of course demands further investigation of the surface system which includes few or even just one 3d transition-metal impurity.

This article theoretically studies magnetism from a single transition-metal atom embedded in the surface layer of Cu(001). A recent study[1] presents that 3d adatoms on the surface of Fe(001) tend to go into the surface layer through a direct exchange mechanism. This then forms an energetically favorable configuration in which a 3d impurity atom takes up the place of a host atom in the surface layer. In our study of the Cu(001) system we intend to calculate the magnetic moment of the impurity in the surface layer. We also like to know whether an impurity atom with large magnetic moment can have any effect on the normally non-magnetic Cu host.

As well known, magnetism is enhanced by the presence of surfaces.[2-4] Cr, for example, is known to have a bulk moment of $0.59\mu_{\rm B}$ per atom. On the Cr(001) surface, which has complicated surface magnetism, the magnetic moment is increased to values that range from $1.75\mu_{\rm B}$ to $2.5\mu_{\rm B}$.[5] Cr thin films on the Fe(001) surface[6-8] have also produced large moments. From $4\mu_{\rm B}$ per atom coming from *in situ* magnetometer measurements to around $1.8\mu_{\rm B}$ by energy-resolved spin-polarized secondary-electron emission, the role of surfaces in the enhancement of magnetism is well established.

As for systems with a single surface impurity atom, a calculation by Lang *et al.*[9] produces a list of magnetic moments of 3d atoms on Cu(001) for both the adatom and in-surface layer position. Their calculation is based on density functional theory and a Korringa-Kohn-Rostoker (KKR) Green's function method for planar defect.[10] By treating the impurity and the first shell of neighboring sites as perturbations, they obtain high magnetic moments for Cr, Mn, and Fe. Others like V and Co also have magnetic moments larger than 1 $\mu_{\rm B}$. There is no mention of magnetism of the neighboring atoms.

Their method makes us worried that a perturbation approach may not be adequate to account for the complicated d-d interaction between the impurity and the host atoms in the surface layer and that self-consistent procedures may not be fully employed to remedy the deficiency. Since a heavy charge exchange is expected on the surface, it seems unlikely that neighboring Cu atoms in the surface layer are unaffected magnetically by the 3d impurity. Magnetization of the Cu atoms, if possible, can be just as important in shaping local magnetism as is the impurity atom.

§2. Calculation Method

We adopted real-space tight-binding linear muffin-tin orbitals (TB-LMTO)[11-14] to calculate the self-consistent spin-polarized density of states for the impurity and its neighbors. This method has been successfully applied to both Cu(110)[15] and Cu(001)[16] surfaces, which are used as the basis for our impurity calculation.

Real-space methods work well with low symmetry systems. Without the artificial imposition of periodic boundary condition along the normal of the surface in $\boldsymbol{k}$ space calculations, the system appears natural and the Hamiltonian can be calculated with a straightforward formulation. However, since the system contains an impurity atom, the Hamiltonian H has two terms H_0 and H_1,

$$H = H_0 + H_1, \tag{1}$$

where H_0 is the Hamiltonian for the host Cu atoms and H_1 is for the impurity atom. Although the equation resembles a perturbation problem, both H_0 and H_1 are adjustable during the self-consistent procedure. Smooth

wave function connections occur between the impurity and host atoms.

To calculate the density of states (DOS), Green's function is defined as the following,

$$G(z) = (z - H)^{-1}, \tag{2}$$

where H is the Hamiltonian of the system, which takes into account the second nearest-neighbor interaction. The DOS $D(E)$ is then derived from the following equation,

$$D(E) = -\frac{1}{\pi} \lim_{\epsilon \to 0} Tr\, \mathrm{I}m\, G(E + \mathrm{i}\epsilon), \tag{3}$$

where Tr $\mathrm{I}m$ denote the trace of the imaginary part of Green's function $G(E + \mathrm{i}\epsilon)$.

Twelve layers were assembled to form the system for calculation, including two empty overlayers which provide sufficient space for wave functions to extend out of the surface layer in a tight-binding scheme. Each layer had thirty two atomic spheres and was considered an infinite plane by imposing a two-dimensional periodic boundary condition. Surface relaxation for Cu(001) was ignored. To date, the only known measurement on the surface relaxation caused by the transition metal impurities is performed on an ordered Cu(001)c(2×2) Mn surface alloy.[17] The results of which, in addition to supplemental calculations, indicate that relaxation has only a slight effect on the magnetic moment of Mn.

§3. Calculated Results

The calculated local magnetic moments for the eight 3d transition-metal impurity atoms in the surface layer of Cu(001) are represented by squares in Fig. 1. The curve connecting those squares closely resembles that presented by Lang *et al.*[9] As is predicted by them, Mn has the largest magnetic moment, followed by Cr and Fe. Differences do arise, however, with the moments for Ti and Ni. Rather than being zero, our calculation put them at 0.16 μ_B and 0.72 μ_B respectively.

Mn has a local moment of $3.36\mu_B$, as presented in Table I, which is slightly smaller than the value given by Lang *et al.* Magnetism becomes stronger if the moment contributions from neighboring Cu atoms are considered. In the surface layer, each of the Cu atoms surrounding the impurity has quite a substantial moment. This ranges from 0.10 μ_B to 0.26 μ_B, which correspond to the eight 3d impurities as shown in Table I and represented by triangles in Fig. 1. These magnetic moments are closely associated with the presence of surface.

If the impurities are located deep in the Cu bulk, contributions of magnetism from surrounding Cu atoms are negligible. Three electronic structure calculations were performed using the same method for each of the three impurities Cr, Mn, and Fe within the bulk of Cu. The local moments for Cr, Mn, and Fe are $3.11\mu_B$, $3.84\mu_B$, and $2.31\mu_B$ respectively. Listed in Table II, the values are in good agreement with the calculation by Braspenning *et al.*[18] The Cu atoms that surround the impurities, whether or not they are in the layer containing the impurities, have at most 0.01 μ_B. Therefore, the location of the impurity is crucial to the magnetism of its neighboring atoms. Within the bulk, the Cu atoms are unaffected magnetically by the impurity, while on the surface neighboring Cu atoms acquire appreciable moments, forming a tiny paramagnetic region centered at the impurity site.

Sharp contrast between the bulk and surface can be observed from another aspect. That is, the charge transfer between the impurity in the bulk and neighboring atoms is generally not significant. Cr, for example, loses less than 0.38 electron per atom, which is shared by its eight nearest neighbors. Mn and Fe lose even fewer

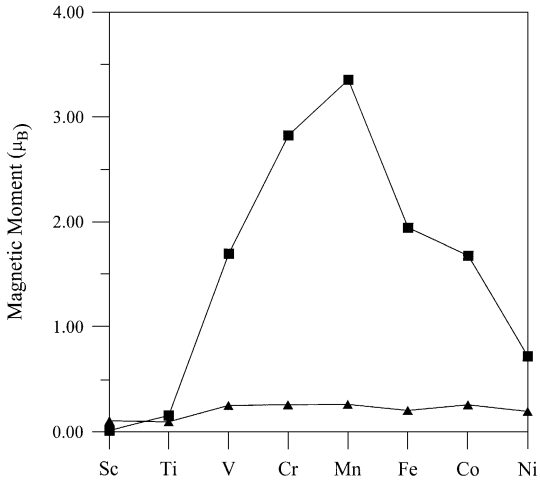

Fig. 1. Distribution of magnetic moments for the eight impurities (squares) and their neighboring Cu atoms (triangles) in the surface layer of Cu(001).

Table I. Magnetic moments for the eight impurities and their neighboring Cu atoms in the surface layer of Cu(001).

Atom	magnetic moment (μ_B)
Sc	0.01
Cu	0.10
Ti	0.16
Cu	0.10
V	1.70
Cu	0.25
Cr	2.83
Cu	0.26
Mn	3.36
Cu	0.26
Fe	1.94
Cu	0.21
Co	1.68
Cu	0.26
Ni	0.72
Cu	0.20

Table II. Magnetic moments for Cr, Mn, and Fe in bulk Cu.

Atom	magnetic moment (μ_B)
Cr	3.11
Mn	3.84
Fe	2.31

Table III. Charge transfers between the impurity atom in the surface layer of Cu(001) and each of its nearest neighbors in the same layer and the layer directly above.

Atomic sphere	Total charge transfer (electrons/atom)
Sc	−1.13
Cu	−0.71
Empty sphere	0.85
Ti	−1.42
Cu	−0.61
Empty sphere	0.82
V	−1.34
Cu	−0.82
Empty sphere	1.01
Cr	−1.24
Cu	−0.85
Empty sphere	1.02
Mn	−1.22
Cu	−0.88
Empty sphere	1.04
Fe	−0.91
Cu	−0.83
Empty sphere	0.91
Co	−0.96
Cu	−0.94
Empty sphere	1.03
Ni	−0.89
Cu	−0.84
Empty sphere	0.91

electrons, 0.35 and 0.20 electron per atom respectively. Charge redistribution on the surface, however, is quite complicated. A reduced coordination number and strong d-d interaction cause heavy charge exchange between the impurity and the surrounding atoms in the surface layer and the empty layer directly above. Major charge transfers that occur between atoms are listed in Table III. Fe, for example, loses 0.91 electron per atom, and each of the surface Cu nearest to Fe loses 0.83 electron per atom while each of the four neighboring empty spheres gains 0.91 electron per atom.

Figures 2(a), 2(b) and 2(c) depict the local DOS of one of the four surface Cu atoms nearest to the impurity Fe for the majority, minority, and combined spins. Two peaks below the Fermi level are identified, −6.67 eV for the majority spin and −4.90 eV for the minority spin. Similar DOS and positions of peaks are also found for Cu atoms surrounding Mn and Cr. Beyond the impurity and the nearest atoms, charge transfer is negligible and magnetism is insignificant. As for each of the four empty spheres nearest to the impurity, the DOS is comprised mostly of s and p waves, which are evenly distributed over both spins. Magnetism is therefore confined within the impurity and its nearest neighbors in the surface layer.

The DOS for the eight impurities is considered with the scanning tunneling microscopy (STM) in mind, since the STM has become a powerful tool for identifying high DOS. From Sc to the end of the 3d series, Ni, the DOS shows consistent shift of electronic states from higher to lower energy. This is due to the fact that generally electrons are more attracted to bigger nuclei. Figures 3(a), 3(b) and 3(c) are DOS for V. More than half of the states for the majority spin and almost all states for the minority spin are above the Fermi level.

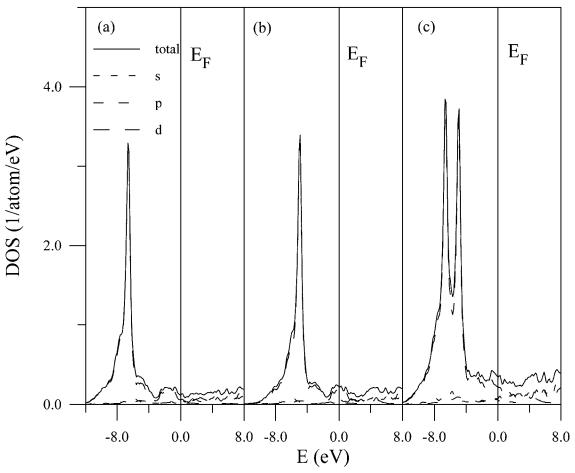

Fig. 2. Local density of states of the surface Cu atoms surrounding the impurity Fe for (a) majority, (b) minority, and (c) both spins.

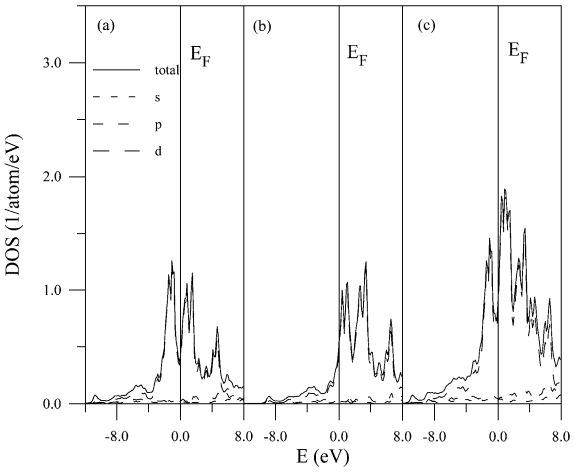

Fig. 3. Local density of states of the impurity V atom in the surface layer of Cu(001) for (a) majority, (b) minority, and (c) both spins.

The Mn impurity has the highest magnetic moment. Its DOS is presented in Figs. 4(a), 4(b) and 4(c) for the majority, minority, and both spins respectively. The two maxima that belong to the majority and minority spin at 3.67 eV below the Fermi level and 0.82 eV above it are identified. They should be detected in the STM spectra and easily distinguished from the host atoms. Mn is also the last of the 3d impurity atoms which have a large portion of electronic states raised above the Fermi level. As we move forward from Mn, the DOS curves have sharper features and positions of peaks are pushed further down the Fermi level. Illustrated in Figs. 5(a), 5(b) and 5(c) are DOS for the Co impurity. At −0.41 eV the minority peak is closer to the Fermi level and should be easily detected experimentally. The majority peak is much lower at −4.63 eV.

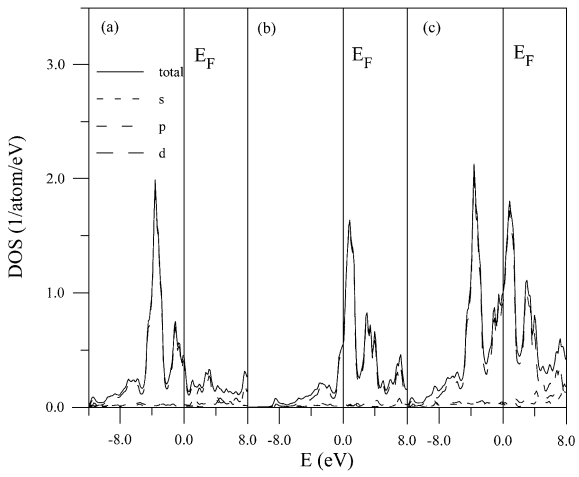

Fig. 4. Local density of states of the impurity Mn atom in the surface layer of Cu(001) for (a) majority, (b) minority, and (c) both spins.

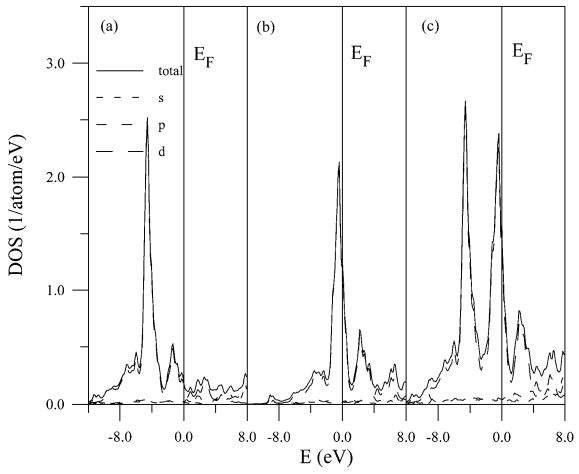

Fig. 5. Local density of states of the impurity Co atom in the surface layer of Cu(001) for (a) majority, (b) minority, and (c) both spins.

§4. Conclusions

By combining TB-LMTO and Green's function, *ab initio* calculations in real space for eight 3d transition-metal atoms from Sc to Ni in the surface layer of Cu(001) were conducted. Strong magnetic moments for some impurities of the series were obtained. Also deduced was that surface Cu atoms nearest to the impurities had substantial magnetism due to the reduced coordination number and strong d-d interaction between them. This induced magnetism, however, did not exist in the bulk of Cu. To study the peculiar magnetism further experimental investigations and calculations are required, which in turn could introduce new applications in surface magnetism.

Acknowledgments

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