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Surface Magnetism of Cu(001) with a Transition-Metal Impurity Atom

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Calculations based on first principles showed that 3d transition-metal atoms can have strong magnetic moments on the surface of Cu(001). Surface magnetism, however, is not limited to the impurities. Substantial moments were also derived from the calculations for surface Cu atoms which are nearest to the impurities. This suggests that the Cu atoms can somehow be "magnetized" at the surface, offering interesting a local magnetism for further exploitation.

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I. Introduction

Materials made of 3d transition metals are associated with magnetism. Technological advancement has generated take great interests in magnetic thin films, especially those made of 3d transition metals such as Cr, Mn, Fe, Co, and Ni. Thin films or multilayers can be grown in many ways, but the growth inevitably starts from the deposition of individual atoms. Following the trend of miniaturization of electronic devices, it should not be long before magnetism from a few atoms is utilized. This, of course, demands more investigations of surface systems, where a few or even just one 3d transition-metal impurity atom is involved.

It has long been confirmed that magnetism may be enhanced due to the presence of surfaces [1-3]. Cr, for example, is known to have a bulk moment of 0.59 μ_B per atom. At the Cr(001) surface, although quite complicated, the moment is increased to values ranging from 1.75 μ_B to 2.5 μ_B [4]. Investigations on Cr thin films on the Fe(001) surface [5-7] have also produced large moments. From 4 μ_B per atom coming from *in situ* magnetometer measurements to around 1.8 μ_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 impurity atom on the surfaces, a calculation by Lang *et al.* [8] produces a list of magnetic moments of 3d atoms on Cu(001) for both adatom positions and in-surface layer positions. Their calculation is based on density functional theory and a Korringa-Kohn-Rostoker (KKR) Green's function method for planar defects [9]. 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 μ_B. There is no mention of magnetism of the neighboring atoms.

Their method vaises a concern 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-consistency may not be put into consideration to remedy the deficiency. Since heavy exchange of charge is normally expected in the surface, it seems unlikely that neighboring Cu atoms in the surface layer are not affected 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.

This article is devoted to theoretical study of magnetism from a single transition-metal atom embedded in the surface layer of Cu(001), which means a configuration in which a 3d impurity atom takes up the place of a host atom in the surface layer. We intend to learn what magnetic moment the impurity may have 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. By using real-space tight-binding linear muffin-tin orbitals (TB-LMTO) [10-13] we are able to calculate self-consistent spin-polarized density of states for the impurity and its neighbors. The method is no stranger to surface calculations. It has been applied successfully to a few metal surfaces [14-17] including both Cu(110) [14] and Cu(001) [15] surfaces, which are used as the basis for our impurity calculation.

Systems with low symmetry are easily treated in real space. Without the artificial imposition of periodic boundary condition along the normal of the surface, as what have been done in **k** space calculations, the system looks natural and the Hamiltonian can be calculated with a straightforward formulation. Since the system has 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. The equation may look like a perturbation problem. In effect, both H_0 and H_1 are capable of doing adjustments in the self-consistent procedure, making smooth connection of wave functions 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 after the orthogonalization. The density of states $D(E)$ is then derived from the following equation,

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

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

A total of 12 layers were assembled to form the system for calculation, including two top empty overlayers which provide enough space for wave functions extending out of the surface layer in a tight-binding scheme. Each layer has 32 atomic spheres and is considered an infinite plane by imposing two-dimensional periodic boundary condition. Surface relaxation for Cu(001) is ignored.The Hamiltonian of the system takes into account the second nearest-neighbor interaction.

Represented by squares in Fig. 1 are the calculated local magnetic moments for the eight 3d transition-metal impurity atoms in the surface layer of Cu(001). We observe a curve connecting

those squares which is very similar to that presented by Lang *et al.* [8] As is predicted by them, Mn has the largest magnetic moment, followed by Cr and Fe. Differences do arise, including the moments for Ti and Ni. Instead of being zero, our calculation put them at 0.16 μ_B and 0.72 μ_B respectively.

Listed in Table I, Mn has a local moment of 3.36 μ_B, which is slightly smaller than the value provided by Lang *et al.* Magnetism is stronger if moment contributions from neighboring Cu atoms are taken into account. In the surface layer, each of the Cu atoms surrounding the impurity has quite substantial moment. Ranging from 0.10 μ_B to 0.26 μ_B corresponding to the eight 3d impurities, as are shown in Table II and represented by triangles in Fig. 1, the magnetic moments are closely associated with the presence of surface.

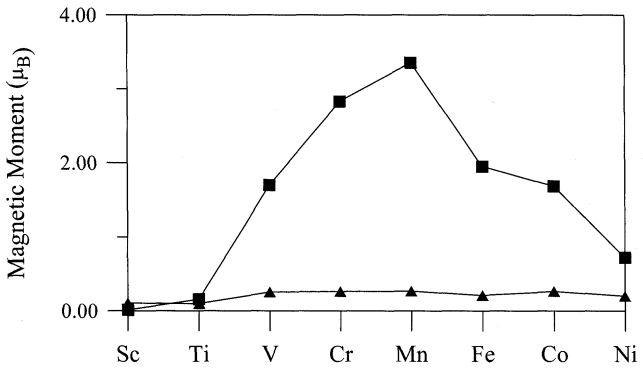

FIG. 1. Distribution of magnetic moments for the eight impurities and their neighboring Cu atoms in the surface layer of Cu(001).

TABLE I. Magnetic moments (μ_B) for the eight impurities in the surface layer of Cu(001).

Sc	Ti	V	Cr	Mn	Fe	Co	Ni
0.01	0.16	1.70	2.83	3.36	1.94	1.68	0.72

TABLE II. Magnetic moments (μ_B) for each of the four surface Cu closest to the eight impurities respectively.

Sc	Ti	V	Cr	Mn	Fe	Co	Ni
0.10	0.10	0.25	0.26	0.26	0.21	0.26	0.20

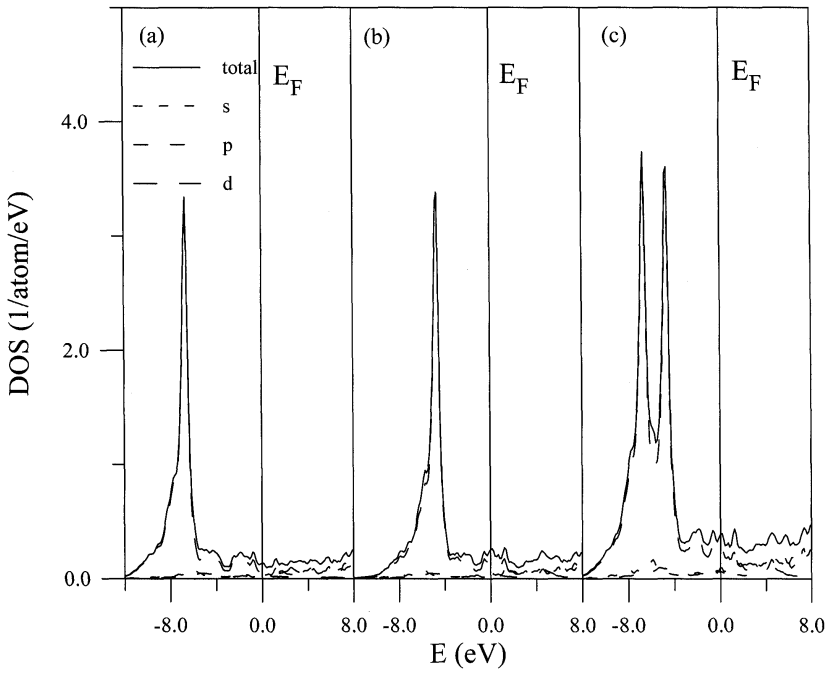

FIG. 2. Local density of states of the surface Cu atoms surrounding the impurity Cr for (a) majority, (b) minority, (c) both spins.

If the impurities are located deep in the Cu bulk, contributions of magnetism from surrounding Cu atoms are negligible. We performed three electronic structure calculations using the same method for each of the three impurities Cr, Mn, and Fe in bulk Cu. The local moments for Cr, Mn, and Fe are 3.11 μ_B, 3.84 μ_B, and 2.31 μ_B respectively. The values are in good agreement with the calculation by Braspenning *et al.* [18]. Those Cu atoms surrounding the impurities in the bulk, whether in the same layer or not, have at most 0.01 μ_B. So it seems that the location of the impurity is crucial in the magnetism of its neighbors. Deep in the bulk Cu atoms are hardly affected at all magnetically by the impurity, while at the surface neighboring Cu atoms acquire appreciable moments, forming a tiny paramagnetic region centered at the impurity.

Enhancement of magnetism for surface Cu atoms may be explained from another aspect. Charge transfer between the impurity in the bulk and its neighbors is generally not pronounced. Cr is found to lose less than 0.38e, which are shared by its eight nearest neighbors. Mn and Fe lose even fewer electrons, 0.35e and 0.20e respectively. Charge redistribution at the surface, however, is quite complicated. Reduced coordination number combined with strong d-d interaction cause heavy charge exchange between the impurity and its immediate neighbors in the surface layer and the empty layer right above. Cr, for example, loses 1.24e, and each of the surface Cu nearest to Cr loses 0.85e while each of the four neighboring empty spheres receives 1.02e.

Figs. 2(a), 2(b), and 2(c) depict the local DOS of one of the four surface Cu atoms nearest to the impurity Cr for the majority, minority, and combined spins. One can identify two peaks below the Fermi level, -6.67 eV for the majority spin and -4.63 eV for the minority spin. Similar DOS and positions of peaks are also found for Cu atoms surrounding Mn and Fe. Beyond the

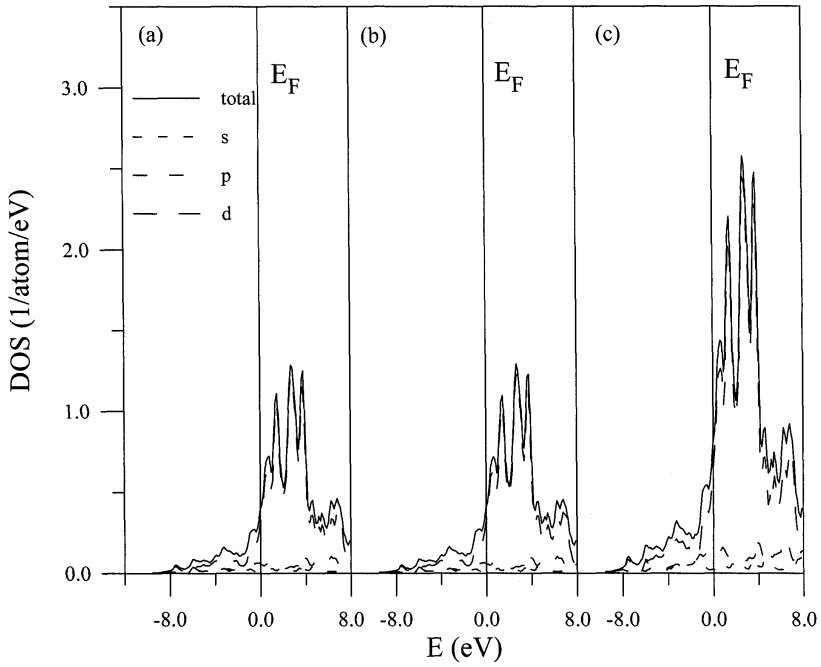

FIG. 3. Local density of states of the impurity Sc atom in the surface layer of Cu(001) for (a) majority, (b) minority, (c) both spins.

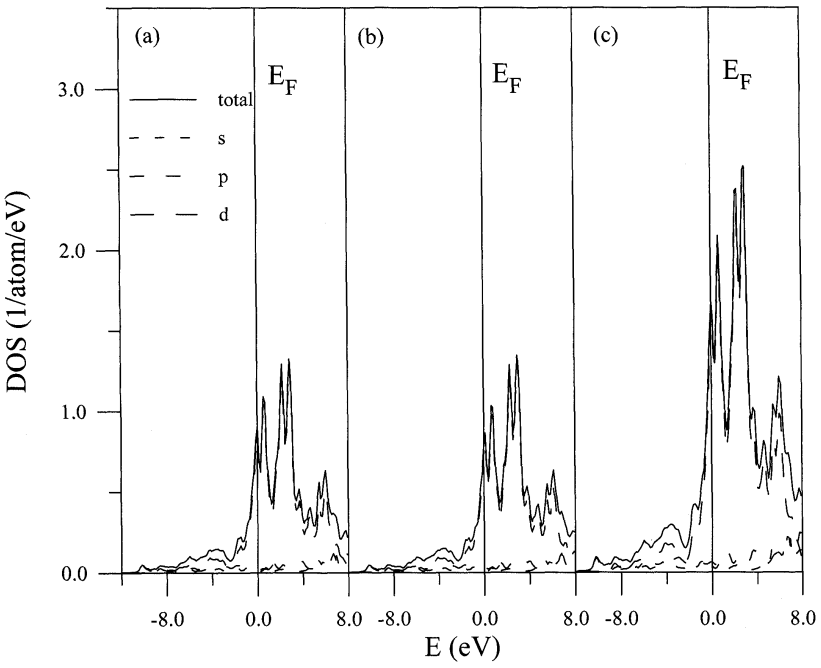

FIG. 4. Local density of states of the impurity Ti atom in the surface layer of Cu(001) for (a) majority, (b) minority, (c) both spins.

impurity and its nearest neighbors, charge transfer is negligible and magnetism is insignificant. As for each of the four nearest empty spheres, the DOS is mostly made up of s and p waves, evenly distributed over both spins. It seems appropriate to say that magnetism is confined within the impurity and its nearest neighbors in the surface layer.

DOS for the eight impurities are an interesting part of the problem, since the scanning tunneling microscopy (STM) has become a powerful tool for identifying high DOS. From the very beginning of Sc to the end of the 3d series, Ni, the DOS shows consistent shift of electronic states from higher energy to lower energy. This comes as no surprise since in general bigger nuclei offer more attraction to electrons. Figs. 3(a), 3(b), and 3(c) are DOS for Sc. Almost all electronic states are above the Fermi level, with negligible split between the majority spin and minority spin. Similar distributions are found for Ti, shown in Figs. 4(a), 4(b), and 4(c), which result in a small magnetic moment.

Beginning with Fe peaks for the majority and minority spins are all below the Fermi level and are sharper to be distinguished. As illustrated in Figs. 5(a), 5(b), and 5(c), two peaks of DOS are found at -0.27 eV and -3.40 eV for Fe. They should be detectable in the STM spectra and easily identified against the host atoms. The same pattern with energies shifted lower can be found for Ni, the last impurity of the series. Two spikes located at -2.72 eV and -4.76 eV respectively are shown in Figs. 6(a), 6(b), and 6(c).

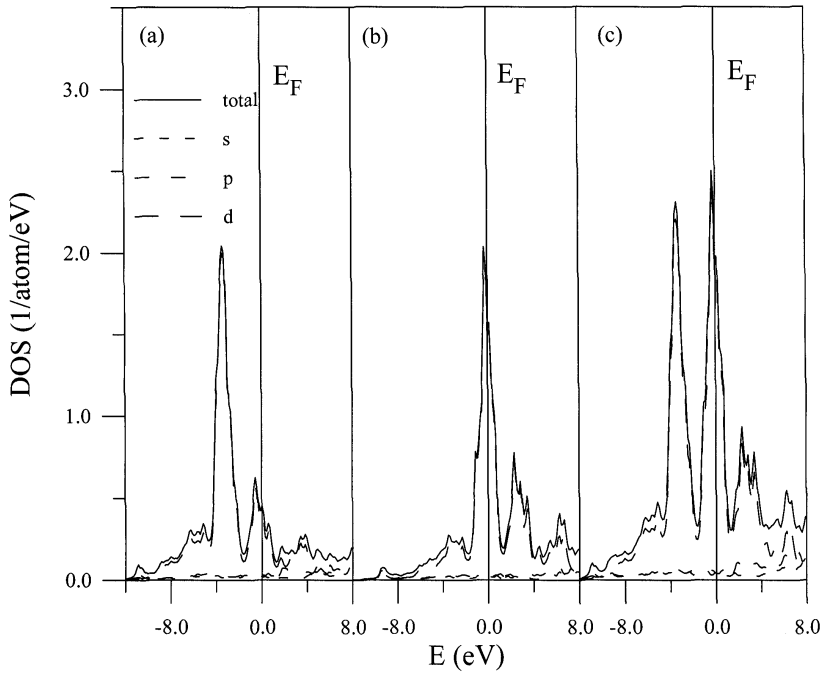

FIG. 5. Local density of states of the impurity Fe atom in the surface layer of Cu(001) for (a) majority, (b) minority, (c) both spins.

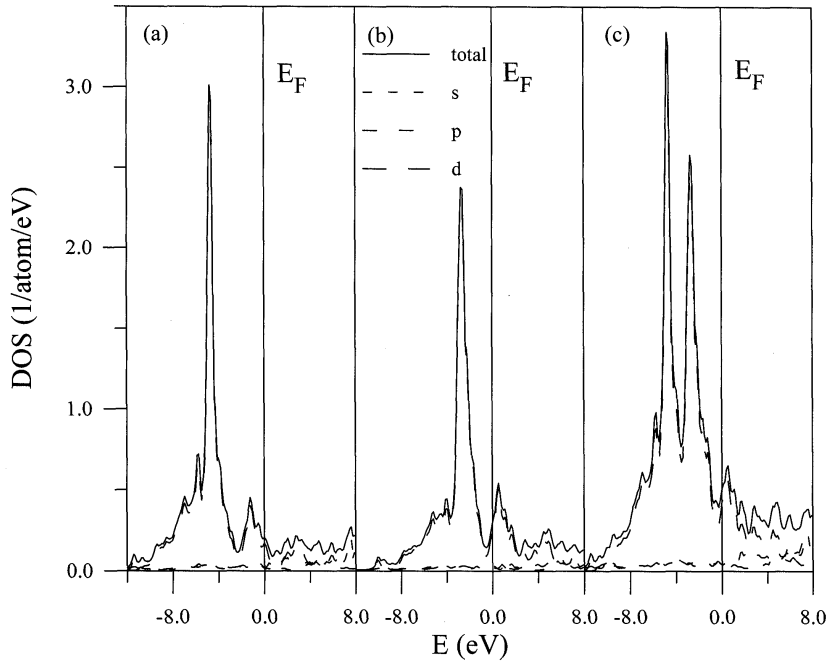

FIG. 6. Local density of states of the impurity Ni atom in the surface layer of Cu(001) for (a) majority, (b) minority, (c) both spins.

In summary, by combining TB-LMTO and Green's function we were able to do *ab initio* calculation in real space for eight 3d transition-metal atoms from Sc to Ni in the surface layer of Cu(001). As expected, we obtained strong magnetic moments for some impurities of the series. We also found that surface Cu atoms nearest to the impurities have substantial magnetism due to the reduced coordination number and strong d-d interaction between them. This induced magnetism cannot be found in the bulk of Cu. Further experimental investigations and calculations are needed to study the peculiar magnetism, which may open up new applications in surface magnetism.

Acknowledgments

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References

[1] C. L. Fu, A. J. Freeman, and T. Oguchi, Phys. Rev. Lett. **54**, 2700 (1985).
[2] L. M. Falicov, R. H. Victora, and J. Tersoff, *The Structureof Surfaces* (Springer, Berlin, 1985).
[3] M. Weinert and S. Blügel, *Magnetic Mutilayers* (World Scientific, Singapore, 1993).
[4] J. A. Stroscio *et al*., Phys. Rev. Lett. **75**, 2960 (1995).
[5] C. Turtur and G. Bayreuther, Phys. Rev. Lett. **72**, 1557 (1994).

[6] P. Fuchs *et al*., Phys. Rev. **B54**, 9304 (1996).
[7] A. Davies *et al*., Phys. Rev. Lett. **76**, 4175 (1996).
[8] P. Lang *et al*., Solid State Commun. **92**, 755 (1994).
[9] R. Zeller *et al*., Mater. Mater. Res. Symp. Proc. **253**, 357 (1992).
[10] O. K. Andersen, Phys. Rev. **B12**, 3060 (1975).
[11] O. K. Andersen, O. Jepsen, and D. Glötzel, *Highlights of Condensed Matter Theory* (North Holland, New York, 1985).
[12] O. K. Andersen, Z. Pawlowska, and O. Jepsen, Phys. Rev. **B34**, 5253 (1986).
[13] H. L. Skriver, *The LMTO Method* (Springer, Berlin, 1984).
[14] C. K. Yang *et al*., Phys. Rev. **B52**, 10803 (1995).
[15] C. K. Yang, J. Phys. Soc. Jpn. **67**, 2055 (1998).
[16] C. K. Yang, Y. C. Cheng, and S. Y. Wu, Chin. J. Phys. **35**, 90 (1997).
[17] C. K. Yang, Y. C. Cheng, and S. Y. Wu, Chin. J. Phys. **53**, 274 (1997).
[18] P. J. Braspenning, R. Zeller, A. Lodder, P. H. Dederichs, Phys. Rev. **B29**, 703 (1984).