Kondo behavior of anisotropic single atomic spins on a Cu_2N molecular layer

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Fitting *ab initio* total energies, obtained within the generalized gradient approximation with spin-orbit coupling and a correction that includes Coulomb repulsion, we calculate the anisotropy parameters D and E of an effective spin model that describes $3d$ magnetic impurities separated from the Cu(100) surface by a monolayer of Cu_2N. Assuming a general exchange interaction between conduction and $3d$ electrons we construct an effective Kondo model which depends on D and E. We discuss the specific cases for Mn, Fe, and Co impurities.

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I. INTRODUCTION

In the last years, there has been a revitalized interest in the Kondo effect, which is exhibited by the localized spin of a magnetic atom when it interacts with the conduction electrons of a nonmagnetic host. This renewed interest in the Kondo associated phenomena, which influence the electronic, thermodynamic, and magnetic properties of interacting systems, has been triggered by the latest applications of scanning tunneling spectroscopy on individual atoms embedded in a superficial molecular network. In particular, experiments have been performed on impurities deposited on a monolayer of Cu_2N grown on Cu(001). The magnetic anisotropy energy and the energy scale of the many-body Kondo interaction are of the same order of magnitude, when the impurities are separated from the metallic host by an insulating layer, such as Cu_2N. The role of this molecular layer is to partially decouple the atomic spin of the deposited magnetic impurity from the underlying metallic surface [in this case Cu(001)] in order to decrease the Kondo interaction to values on the order of magnitude of the anisotropy energy.

The magnetic excitations of one or a few magnetic atoms have been recently studied using inelastic electron tunneling spectroscopy (IETS).[1–5] In the absence of the Kondo effect, the observed differential conductance dI/dV can be interpreted with a spin-assisted tunneling Hamiltonian.[6] At low voltages V, a Kondo resonance appears in the case of magnetic atoms with large spins whenever the magnetic anisotropy of the system gives rise to a doublet ground state corresponding to an effective spin-1/2 system, and both states of the doublet are coupled by a spin flip with the conduction electrons of the host.[3,5] The latter is always the case when in addition to the longitudinal magnetic anisotropy DS_z^2, the transverse anisotropy $E(S_x^2-S_y^2)$ is also present.[7,8]

The goal of this contribution is twofold. On the one hand, we are interested in the density-functional theory (DFT) calculation of the anisotropy constants at the impurity site for $3d$ magnetic impurities deposited on the above-mentioned molecular network and in the comparison of the obtained results with experiments and with previous calculations. On the other hand, we are interested in studying the influence of the magnetic anisotropy on the appearance or inhibition of the Kondo effect in the systems. The $3d$ impurities considered are Mn, Fe, and Co.

The anisotropy constants of the studied systems have been previously determined by Shick *et al.*[9] who performed DFT calculations and used the torque method[10] in order to obtain the constants. In this contribution, we use GGA+U to obtain the electronic structure and total energies and use a procedure simpler than the torque method to determine the anisotropy constants. The procedure is being described below.

The Kondo temperature, T_K, of Co deposited on Cu_2N has already been determined using IETS (Ref. 4) while experiments point toward Kondo temperatures of Mn and Fe that are either lower than the experimentally achievable temperatures or nonexistent, due to an eventual nondegenerate ground state. We assume the same exchange constant for the interaction between the electron spins of any of the $3d$ impurities with the spin of the conduction band and construct an effective Kondo model for the low-energy physics. Actually, using the experimentally obtained value for the T_K of Co and the DFT calculated anisotropy constants (axial and transverse contributions), we derive an effective anisotropic Kondo Hamiltonian to describe the three impurity systems and to estimate the Kondo temperatures of the two other magnetic impurities of our interest (Mn and Fe).

The paper is organized as follows. In Sec. II, we present the details of the calculations and the results obtained from them for the effective anisotropy parameters. In Sec. III, we describe the effective Kondo model and the equations and approximations used to estimate the Kondo temperature. Section IV contains a summary.

II. MAGNETIC ANISOTROPY

In order to obtain the magnetic anisotropy we perform DFT spin-polarized electronic calculations using the full potential linearized augmented plane waves method as implemented in the WIEN2K code.[11] The generalized gradient approximation (GGA) for the exchange and correlation potential in the parametrization of Perdew, Burke, and Ernzerhof is used.[12]

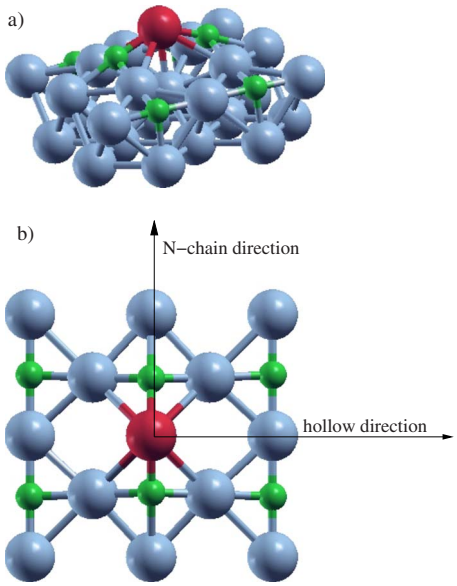

FIG. 1. (Color online) (a) Relaxed structure of an adatom deposited on a Cu_2N layer on top of a Cu(001) substrate. Only the outermost two layers are represented. Cu, N and transition-metal atoms are depicted by large gray (blue online), small gray (green online), and black spheres (red online), respectively. (b) Top view of the same structure.

We do supercell calculations and simulate the studied systems with slabs. The slabs consist of three Cu layers grown along the (001) direction. On both sides of these slabs, a single Cu_2N layer is arranged. The in-plane surface unit cell is twice as large as the one of Cu_2N and the impurity atoms, Mn, Fe, and Co, are located on top of a Cu atom. The empty space in between periodically repeated slabs is 13.8 Å.

We use the augmented plane wave-local orbital (apw-lo) basis.[11] The cut-off parameter RK_{max}, which determines the number of plane waves in the interstitial region, is taken as 8. Here R is the minimum muffin-tin radius in the corresponding cell and K_{max} is the length of the largest wave vector of the interstitial plane waves. The muffin-tin radii used are $R_{MT}^{N}=1.59$ bohr, $R_{MT}^{Mn}=1.85$ bohr, $R_{MT}^{Fe}=1.84$ bohr, $R_{MT}^{Co}=1.82$ bohr, and $R_{MT}^{Cu}=1.79$ bohr.

To account for the localization of the d valence orbitals of the impurities, we go beyond GGA including an U Hubbard term, that is GGA+U. Among the different possibilities for the GGA+U approach, we use the self-interaction correction variant.[13] For the effective values of U, we take 5 eV for Mn,[3] 2 eV for Fe,[9] and 2 eV for Co.[14]

The considered structures are minimized without taking into account spin-orbit coupling using 200 k points in the first Brillouin zone. The final atomic configuration for each system under study is obtained by allowing to relax until the residual forces are less than 0.10 eV/Å. In Fig. 1(a), we show one of the relaxed structures. The atomic positions are similar to the ones of Refs. 9 and 14. The Cu atom beneath the adatom undergoes an inward relaxation resulting in a distance between them of 2.41 Å for Mn, 2.36 Å for Fe, and 2.31 Å for Co. Besides, the two nearest-neighbor N atoms of an adatom relax outward. In the three systems, the N positions are very similar. These are the major observed trends. The other atoms in the surface undergo slight displacements.

TABLE I. Difference between the total energy in millielectron volt for "hollow" or "perpendicular," and "chain" directions of the magnetization for the three systems studied.

MAE (meV)	Mn	Fe	Co
E[hollow]−E[chain]	−0.2	1.5	2.0
E[perp]−E[chain]	−0.2	0.8	0.3

To obtain the magnetic anisotropy energies (MAEs), the spin-orbit interaction is included within the self-consistent second variational approach as implemented in the above-mentioned code. We consider 800 k points in the first Brillouin zone. Following the experimental reports, we calculate total energies for the magnetization axis lying along three inequivalent directions, one of them perpendicular to the surface and two in-plane ones. One of the in-plane directions points along neighboring hollow sites of the impurity. It is the so-called *hollow direction* in the literature. The other in-plane direction is perpendicular to the previous one and is the so called N-*chain direction*, as it corresponds to the direction given by the N chains of the surface. See Fig. 1(b).

In Table I, we present the total-energy difference between the three quantization directions for the different adatoms in millielectron volt. In the case of a Co impurity, the system shows an in-plane hard axis lying along the *hollow direction* in agreement with the experimental results. In the case of Fe, our calculations give an easy magnetization axis along the N-*chain* direction, again in agreement with the experiments.

For the Mn impurities, we observe a decrease in the absolute values of the MAE due to the half-filled 3d band and from the numerical results, one would conclude that the system has an easy plane determined by the perpendicular to the surface and the *hollow direction*. Experimentally, what is being reported is that there is an easy axis perpendicular to the surface. Note that for the three magnetic impurities, Mn, Fe, and Co the differences in energies obtained are near to those obtained previously in Refs. 9 and 14. In the case of Co, the cited references had already included the Coulomb U repulsion through GGA+U. In the case of Mn, our use of GGA+U does not change significantly the theoretical results. The reason for the discrepancy between theory and experiment in the case of Mn is at present not clear to us. It might be that the small energy differences in this case are near the limit of accuracy of our calculations. Another possibility is that below 0.2 meV, the details of the different interaction terms among d electrons[15] become important and the GGA+U as implemented does not account for that.

From the energies obtained for the different quantization axis, the coefficients of the anisotropy Hamiltonian are derived. We consider the anisotropy Hamiltonian given in the usual form,

$$H_{\text{aniso}} = DS_z^2 + E(S_x^2 - S_y^2). \quad (1)$$

The first term gives the axial magnetic anisotropy and the second one is the transverse contribution to it. We apply the

TABLE II. Directions that maximize $|D|$ and give positive E, and corresponding values of D and E in millielectron volt for each impurity.

	Mn	Fe	Co
x	Perp	Hollow	Perp
y	Hollow	Perp	Chain
z	Chain	Chain	Hollow
D	0.04	−0.37	1.23
E	0.00	0.12	0.10

usual convention, namely, that the z axis is chosen in such a way that $|D|$ is maximized and the x and y axes are oriented in order to provide that $E>0$. Within this convention if D is less than zero, the z axis is an easy axis while a positive D means that the z axis is a hard one (easy plane).

To obtain the parameters of H_{aniso}, we map the DFT ground states obtained with the impurity spins pointing in the directions $\alpha=x$, y or z, into the corresponding states $|S,\alpha\rangle$ of a spin S. Using rotation matrices,[16] these states can be written as

$$|S,z\rangle = |S,S\rangle,$$

$$|S,x\rangle = 2^{-S}\sum_{M}\sqrt{\frac{(2S)!}{(S+M)!(S-M)!}}|S,M\rangle,$$

$$|S,y\rangle = 2^{-S}\sum_{M}\sqrt{\frac{(2S)!}{(S+M)!(S-M)!}}e^{-iM\pi/2}|S,M\rangle. \quad (2)$$

The three energies coming from the DFT calculations correspond to $E_\alpha=\langle S,\alpha|H_{\text{aniso}}|S,\alpha\rangle$. From these three energies, the constants D, E and an irrelevant additive constant are determined. The resulting values for the three impurity systems considered and the labeling of the coordinate axis according to the usual convention (see above), are listed in Table II.

Our results are consistent with those reported previously by Shick *et al.* using the torque method to obtain the anisotropy parameters.[9,14] For the case of Mn, these authors report $D=-E=-0.03$ meV but using a different convention for the coordinate axis.[14] By interchanging the x and z axis, it is easy to see that the resulting anisotropy Hamiltonian in the example of Ref. 14 is equivalent to one with $D=0.06$ meV, $E=0$, within the usual convention that we have followed. This agrees with our result except for a factor 3/2 (see Table II). However, this result does not fully reproduce the experimental one.[3] Our results for Fe are in quantitative agreement with those reported by Shick *et al.*[14] In this case, while the signs of the anisotropy parameters coincide with those reported experimentally, the latter are nearly four times larger than the theoretical ones. A similar situation takes place for Co, for which our theoretical results are nearly half the experimental ones.[4] The results obtained by Shick *et al.* for Co,[9] although they depend on the particular DFT method used, are also consistent with our results and with the signs of the experiments. The possible reasons for the discrepancy of theory and experiment in particular in the case of Mn are discussed in Sec. IV.

In the next section, we use the calculated information to discuss the possible Kondo behavior.

III. KONDO BEHAVIOR

To describe the Kondo physics, we start from a rather general Kondo model, in which a band of spin-1/2 conduction electrons interact with all $3d$ electrons of the impurity. The starting Hamiltonian is written as

$$H = H_{\text{aniso}} + H_{\text{band}} + H_K, \quad (3)$$

where the second term describes the conduction band,

$$H_{\text{band}} = \sum_{k\sigma}\epsilon_k c^\dagger_{k\sigma}c_{k\sigma}, \quad (4)$$

and the last one represents the Kondo interaction,

$$H_K = J_1\sum_j \vec{S}_j\cdot\vec{s}, \quad (5)$$

where $\vec{S}_j=\frac{1}{2}\Sigma_{\alpha,\beta}d^\dagger_{j\alpha}\vec{\sigma}_{\alpha\beta}d_{j\beta}$ is the spin of the electron at the d orbital of type (symmetry) j, and $\vec{s}$ is the spin of the conduction electrons at the site of the impurity ($\vec{s}=\frac{1}{N}\Sigma_{k\alpha\beta}c^\dagger_{k\alpha}\vec{\sigma}_{\alpha\beta}c_{k\beta}$). We consider that the exchange constant J_1 is independent of wave vector k, that it is isotropic in the spin space, and that it is approximately constant along the $3d$ series. Using Hunds' rules, the above interaction can be written in terms of the total spin $\vec{S}$ at the impurity site as $H_K=J\vec{S}\cdot\vec{s}$, where $J=J_1/2S$.[17] The values of the total spin used are $S=3/2$, 2, and 5/2 for Co, Fe, and Mn, respectively, in agreement with the values suggested by the GGA+U calculations. These values are consistent with the dominance of Hunds' rules in comparison with crystal-field effects.

For Fe, all eigenstates of H_{aniso} are nondegenerate and therefore there is no Kondo effect. For Co and Mn, we find that the ground state of H_{aniso} is a doublet. In these last two cases, Mn and Co, we project H_K on the ground-state doublet, obtaining an effective anisotropic spin-1/2 Kondo Hamiltonian,

$$H_K = \frac{1}{2}\sum_\alpha J_\alpha\sigma_\alpha s_\alpha, \quad (6)$$

where here σ_α, $\alpha=x,y,z$ are Pauli matrices acting on the effective spin $\frac{1}{2}$, which is the ground state of H_{aniso}. The values of J_α are found identifying the matrix elements of Eq. (5) in the Hilbert subspace which contains only the ground-state doublet of H_{aniso}, with the corresponding matrix elements of Eq. (6).

To estimate the Kondo temperature T_K of this model, we replace J_x and J_y by their average $J_\perp=\frac{J_x+J_y}{2}$ and use[7]

$$T_K = W\exp\left(-\frac{\arctan\gamma}{\gamma\rho J_z}\right), \quad (7)$$

where $\gamma=\sqrt{(\frac{J_\perp}{J_z})^2-1}$, and we take $W=20$ eV from the width of the s bands coming out of our DFT calculations. $\rho=\frac{1}{W}$ is the density of states.

Assuming that for Co, $T_K=2.6$ K, as reported experimentally,[4] we obtain $J_1=2.97$ eV from Eq. (7). Taking this value and using the above formalism, we can predict the value of the Kondo temperature for other $3d$ impurities for which the anisotropy parameters are known. In particular, for Mn, taking the experimentally reported vales for D and E, we obtain a negligible small T_K (on the order of 10^{-10} K). This value is however very sensitive to the ratio E/D. Taking instead our theoretical values we obtain, using this approach, $T_K=0.1$ K. This value is less than the temperature achieved in the experiments (0.5 K). It is clear then, that a Kondo effect cannot be ruled out solely on the basis of reported tunneling experiments.

IV. SUMMARY

Using total energies coming from GGA+U calculations, we obtained the parameters that describe the magnetic anisotropy of Mn, Fe, and Co impurities on a layer of Cu_2N deposited on Cu(111). The obtained anisotropy parameters for Fe and Co agree well in sign and order of magnitude with the experimental values. In the case of Mn, our results indicate that the energies corresponding to the magnetization of Mn pointing in the hollow direction and in the direction perpendicular to the surface plane are very similar, and lower by 0.2 meV than when pointing in the N-chain direction. To obtain agreement with the experiments, one would have to shift up the energy corresponding to the magnetization in the hollow direction, in such a way that it should be nearly degenerate to the magnetization in the direction of the chain of N atoms, converting a hard axis in the chain direction into an easy axis in the perpendicular one. This discrepancy might be due to the lack of enough accuracy in our calculations. Another possibility is that at this energy scale, the details of the correlations become important and that it is not enough to include them in an average way as in LDA+U or GGA+U. In the presence of crystal field or anisotropy effects, the interactions between d electrons in different orbitals are very involved.[15]

From the information obtained of the DFT calculations, we conclude that the system containing Fe impurities does not exhibit Kondo effect since the ground state in the absence of the exchange interaction J_1 is non magnetic. Instead, the systems with Co and Mn impurities can be described by an effective anisotropic Kondo model. Getting J_1 from the observed Kondo temperature corresponding to the Co impurity and, assuming that this interaction is rather independent of transition-metal element along the $3d$ series, we predict for Mn a negligible Kondo temperature, when using the experimentally determined values for the anisotropy parameters D and E. Using instead, our calculated D and E values we obtain $T_K=0.1$ K, which is lower than the temperature at which the experiments have been performed. However, we believe that the experimental analysis is robust and therefore an observable Kondo effect for Mn is unlikely. The theoretical prediction is affected by shortcomings discussed earlier in the calculation of the anisotropy parameters.

For the prediction of T_K, the signs of the anisotropy parameters E and D and their ratio are important while their order of magnitude is irrelevant as long as D is larger than T_K.

Just to conclude, it must be pointed out that our formalism can be easily extended to other impurities.

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