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Co impurities on Ag and Cu: Kondo temperature dependence on substrate orientation

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The surface Kondo effect of a single Co impurity adsorbed on different noble-metal surfaces is revisited. The magnetic system mapped onto the Anderson impurity model is solved within standard noncrossing approximation techniques using data coming from electronic structure calculations. The observed experimental trends of the Kondo temperature are explained in terms of the particular features of the hybridization function and of the d impurity level position.

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The coupling between a localized spin and its environment is a general problem of fundamental interest and arises in a number of physical situations. One important example is the Kondo effect, which was originally studied in the context of a magnetic impurity embedded in a bulk, nonmagnetic metal.[1,2] Within the Kondo theory, the quantum-mechanical coupling between the conduction-band electrons of a host metal and the unpaired electrons of an impurity atom due to spin-flip scattering processes leads to a many-body electronic ground state, with the conduction-electron spins aligned to screen the local spin of the impurity. Below a characteristic temperature T_K, the formation of this Kondo ground state is signaled by the appearance of a sharp resonance in the local density of states near the Fermi energy, E_F, at the impurity site, whose width is proportional to T_K.

Using scanning tunneling spectroscopy (STS), it is possible to directly probe the Kondo effect originated at individual magnetic impurities on metallic surfaces.[3,4] The Kondo resonance appears as a feature described by a Fano line shape in the STS spectra,[5] and its shape and width give insight into the tunneling processes through the impurity and determine the Kondo temperature of the system. Consequently, in the last decade, intensive research on this kind of phenomena has been done both theoretically and experimentally. Nowadays, the Kondo effect is being investigated for a number of different magnetic adatoms deposited not only on metallic surfaces[6–12] but also within artificial nanostructures such as quantum corrals[8,13] and molecules.[14,15] In more recent experiments, it has also been shown that it is possible to control the characteristics, and even the existence, of the Kondo resonance by modifying the chemical surroundings of magnetic atoms[14,16–18] and to exploit the Kondo effect as a local probe to determine the exchange interaction between individual adatoms on a metallic substrate as a function of their distance.[19]

In this work, we are going to revisit the Kondo problem of Co impurities on noble-metal substrates, in particular Co adatoms on Cu(001), Cu(111), Ag(001), and Ag(111). This study is motivated by experimental results which show different T_K behaviors for the mentioned surfaces, as summarized in Table I. It can be seen that the Kondo temperature of a Co impurity on Cu is higher for the (001) surface than for the (111) surface, while the contrary is observed for Ag. In this work, we want to contribute to the understanding of the different trends observed.

To address the above-mentioned study, we use a mixed calculation technique and the results of electronic structure calculations are used as input for the Anderson impurity model. From the *ab initio* calculations we obtain the Co impurity d filling to be used in the construction of an effective many-body model. We also obtain the relaxed positions of the impurity for each substrate, information which is used to calculate the hybridization function of the d orbitals of the Co adatoms with the substrate states.

We start by calculating the electronic structure for each system using the all-electron full-potential linearized augmented plane wave (LAPW) method within the density-functional theory, as implemented in the WIEN2K code,[20] with the exchange-correlation potential as given in the generalized gradient approximation.[21] The systems are modeled by supercells composed by five layer slabs separated by six vacuum layers in each case. The thickness of the vacuum region between slabs is found to be enough to avoid interactions between atoms of different slabs. Within each unit cell, there are eight or nine noble-metal atoms per layer for the (001) and (111) surfaces, respectively, and a Co adatom is placed in a fcc hollow position on the slabs' surfaces. We consider that the lateral distance between Co impurities is large enough to avoid coupling among them because the local density of states (LDOS) and the d occupation of Co do not change with larger impurity dilutions.

TABLE I. Shown are the relaxed vertical distances h between Co adatoms and the noble-metal surface, the Co d-orbital occupations n_d, and the experimental Kondo temperatures, T_K^{exp}.

Substrate	h (a.u.)	n_d (eV)	T_K^{exp} (K)
Cu(001)	3.03	7.11	88 ± 4[a]
Cu(111)	3.53	7.11	54 ± 2[a,b]
Ag(001)	3.13	7.10	41 ± 5[c]
Ag(111)	3.81	7.10	92 ± 6[d]

[a] Reference 9.
[b] Reference 8.
[c] Reference 7.
[d] Reference 10.

The relaxed positions of the Co impurities on each of the surfaces are calculated by minimizing the total energy. In Table I, we give the obtained perpendicular distance, h, of Co to each surface after relaxation. As the (111) surface is more closely packed than the (001) surface, the Co adatom is adsorbed at a larger height in the former than in the latter case.

The surface Kondo effect can be described by the Anderson impurity model[22] given by

$$\hat{H} = \sum_{\mathbf{k}} \epsilon_{\mathbf{k}} \hat{c}^{\dagger}_{\mathbf{k},\sigma}\hat{c}_{\mathbf{k},\sigma} + \sum_{m} \epsilon_{m,\sigma}\hat{d}^{\dagger}_{m,\sigma}\hat{d}_{m,\sigma} + \frac{U}{2}\sum_{(m,\sigma)\neq(m',\sigma')} \hat{d}^{\dagger}_{m,\sigma}\hat{d}_{m,\sigma}\hat{d}^{\dagger}_{m',\sigma'}\hat{d}_{m',\sigma'} + \sum_{\mathbf{k},m,\sigma} (V_{\mathbf{k},d_m}\hat{d}^{\dagger}_{m,\sigma}\hat{c}_{\mathbf{k},\sigma} + V_{\mathbf{k},d_m}\hat{c}^{\dagger}_{\mathbf{k},\sigma}\hat{d}_{m,\sigma}), \qquad (1)$$

where the first term represents the kinetic energy of the substrate electrons, $c^{\dagger}_{\mathbf{k},\sigma}$ creates a conduction electron with spin σ and momentum $\mathbf{k}$, and $\epsilon_{\mathbf{k}}$ is the corresponding eigenenergy. $\epsilon_{m,\sigma}$ is the energy level of an electron with spin σ residing in a d_m orbital of the impurity, and $d^{\dagger}_{m,\sigma}$ creates an electron with spin σ in this impurity orbital. U is the on-site Coulomb repulsion between two electrons in any of the impurity levels, and $V_{\mathbf{k}d_m}$ are the hybridization matrix elements between the substrate and the adatom.

The Kondo effect being a many-body phenomenon, results from one-electron calculations cannot be directly related to low-energy excitation dynamic features. But, from these calculations, we can determine static quantities such as the average impurity occupation number, n_d.[23] In Table I we give the Co d-orbital occupations, n_d, for the different substrates.[25] For all the systems, $n_d \approx 7$. Hund's exchange J is on the order of 1 eV in the case of Co, whose value is commonly accepted in the literature, and it is normally not much affected by solid-state screening.[24] From the d LDOS of the impurity, the crystal-field splittings on noble metals lie in the range of 0.2–0.3 eV and are smaller than J. Hund's exchange overweights, then, crystal-field effects, and thereafter we consider an effective Anderson Hamiltonian with degeneracy, N, equal to 4. This corresponds to $S=3/2$ ($N=2S+1$).

To solve the Hamiltonian, we use the standard noncrossing approximation (NCA), with finite U including vertex corrections.[26–29] The inputs for this Hamiltonian are the hybridization function $\Gamma(\varepsilon)$, ϵ_m, and U. We want to understand the trends of T_K in terms of the different hybridization functions and as a function of the relative position of the Co d levels for the different surfaces, ϵ_m.

The average hybridization function $\Gamma(\varepsilon)$ is given by[30]

$$\Gamma(\varepsilon) = \frac{1}{10}\lim_{\eta\to 0}\sum_{\mathbf{k},m} \mathrm{Im}\frac{|V^2_{\mathbf{k}d_m}|}{(\varepsilon + i\eta - \epsilon_{\mathbf{k}})}, \qquad (2)$$

where $\epsilon_{\mathbf{k}}$ are the energies of the eigenstates, $|\mathbf{k}\rangle$, of the clean surface, without Co impurities, and, $|d_m\rangle$ denotes the Co atomic orbitals. $V_{\mathbf{k}d_m} = \langle \mathbf{k}|H|d_m\rangle$ is the effective hopping between substrate conduction states and impurity d orbitals. In our approach, this function for each system is obtained by solving a well-fitted tight-binding Hamiltonian as it has been explained in Ref. 30. We first obtain the eigenstates $|\mathbf{k}\rangle$ for the clean surfaces simulated by slabs containing 18 layers.[30] Then, a Co adatom is introduced, and we obtain the effective hoppings $V_{\mathbf{k}d_m}$ by performing a change in basis. The relaxed positions of the adatom in each case are taken into account through the values of the effective hopping elements between the impurity d levels and the corresponding eigenstates of the clean surfaces.[31,32] It is interesting to point out that relaxation leads to enhanced impurity-substrate hybridizations.

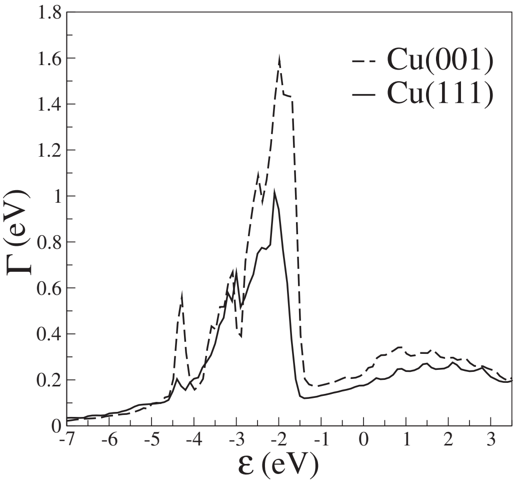

FIG. 1. Hybridization function of impurity Co d orbitals with the Cu substrate states for the (001) and (111) surface orientations. Energies are given with respect to the Fermi level.

In Figs. 1 and 2 we show the hybridization functions for the different systems under study obtained using Eq. (2). The hybridization function shows a rich structure in the energy region where the respective substrate d bands are located. The d bands of Ag lie lower in energy than the Cu ones, and that is clearly reflected in $\Gamma(\varepsilon)$. In the energy range corresponding to the hybridization of the d impurity levels with the substrate d bands, $\Gamma(\varepsilon)$ is far from being constant. Outside this region and near to the Fermi level, the hybridization

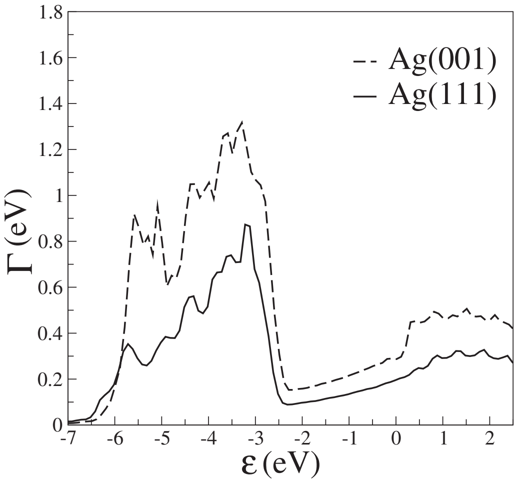

FIG. 2. Same as in Fig. 1 but for Ag.

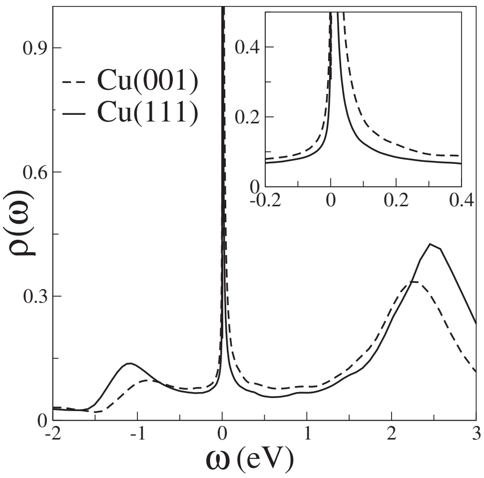

FIG. 3. Spectral functions for Co on Cu(001) and on Cu(111). The inset shows in detail the resonance peak for each orientation.

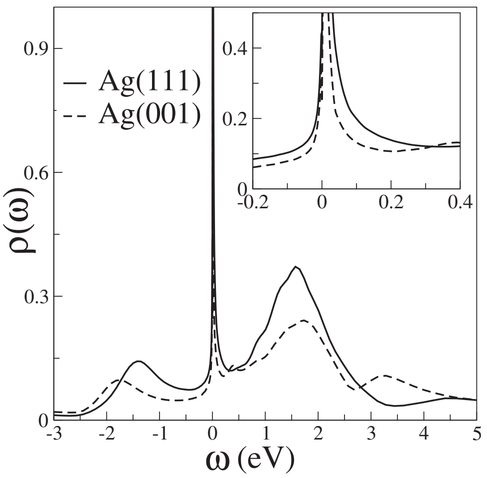

FIG. 4. Same as in Fig. 3 but for Ag.

is given mainly with the *sp*-like states of the substrate, and it could be approximated by a flat, shapeless function. As expected, $\Gamma(\varepsilon)$ is larger for the (001) surfaces than for the (111) ones because the impurity has a larger coordination number in the first case. The structure-rich region of $\Gamma(\varepsilon)$ has a width given by the surface *d* band of the substrate, which depends on the number of nearest neighbors for each orientation [eight for the (100) and nine for the (111)] and on the strength of the interatomic hopping interactions between substrate and impurity.

With respect to the Coulomb repulsion, U, of the impurity *d* levels it should be larger than in the bulk. When solving the NCA equations we consider then different values of U within the range of 2.5–4 eV. For the last parameters of the model, ϵ_m, we take for each system a unique value and call it, from now on, ϵ_d. These impurity ϵ_d values are fitted in order to reproduce the experimental T_K's of the different surfaces. From the resolution of the Anderson model we obtain the spectral functions of the Co *d* electrons. As in Ref. 26 we define T_K as the position of the Kondo resonance with respect to the system's Fermi energy at low temperature. On the other hand, the outcoming half-width of the Kondo resonance is proportional to the value of T_K, as it should be. Within the above-mentioned energy range for U, the fitted ϵ_d's for each system do not change significantly. We show in Figs. 3 and 4 the spectral functions obtained at 5 K, for $U = 4$ eV; the fitted ϵ_d values are shown in Table II. From these figures, it can be seen that the narrow Kondo resonance clearly appears in between the two Hubbard bands and that its half-width follows the experimental trends.

To separate the effects of hybridization and impurity *d* energy-level position, ϵ_d, on the value of T_K, we first assume the same value of ϵ_d for all the systems and focus in this way on the effect of the hybridization function. Under these conditions, we obtain that the T_K values for the (001) surfaces are higher than the ones for the (111) for both substrates. This behavior is independent of the value used for ϵ_d within a wide energy range going from -2.5 to -0.5 eV. This is due to the fact that $\Gamma(\varepsilon)$ for the (001) surfaces is larger than for the (111) in the whole energy range (see Figs. 1 and 2). This is consistent with a larger number of noble-metal nearest neighbors of the Co impurity for the first orientation. A higher degree of hybridization leads to a higher T_K. This is experimentally observed for Cu, but it is not the trend observed in the case of Ag. To understand this one has to go beyond the hybridization dependence and has to take into account the impurity *d* level shifts induced by the substrate potential. It is interesting to compare the fitted ϵ_d values with the energy of the impurity *d* band centers, E_d, obtained from our *ab initio* calculations. The sequence in the ordering of these energies is $E_d^{\mathrm{Ag}(001)} \leq E_d^{\mathrm{Cu}(001)} \leq E_d^{\mathrm{Cu}(111)} \leq E_d^{\mathrm{Ag}(111)}$, which agrees with the ordering of the fitted ϵ_d's, as it can be seen in Table II. Moreover, the difference in energy between the fitted ϵ_d values for the (001) and (111) orientations, $\epsilon_d^{(001)}$ and $\epsilon_d^{(111)}$, for the Ag substrate is larger than the same difference in the case of Cu. This is due to the larger effective Ag potential and agrees well with what happens to the corresponding differences among the *ab initio* calculated *d* band centers. These shifts are of electrostatic origin, and the magnitude of the site energy differences is to be related to the different number of nearest neighbors of the impurity in the (001) and (111) surfaces.

For a flat hybridization an increasing value of $|\epsilon_d|$ leads to a decreasing T_K. This is precisely what happens in the case of Ag. ϵ_d falls in a region where $\Gamma(\varepsilon)$ is nearly flat and has similar values for the two orientations. In spite of a larger $\Gamma(\varepsilon)$ for the (001) surface, which should favor a larger T_K at equal ϵ_d's, the effect of the energy shift is more important and leads to a larger T_K for the (111) surface in this case. For Cu, even if the ϵ_d shifts follow the same ordering as for Ag, the difference in energy between surface orientations is smaller, and $\Gamma(\varepsilon)$ for values of ε around ϵ_d has a rich struc-

TABLE II. Shown are the fitted *d* impurity levels, ϵ_d, that reproduce the experimental T_K's and the Co *d* band centers, E_d, coming from *ab initio* calculations on the different substrates.

System	Co/Cu(111)	Co/Cu(001)	Co/Ag(111)	Co/Ag(001)
ϵ_d (eV)	−1.8	−2.0	−1.6	−2.1
E_d (eV)	−2.1	−2.2	−2.0	−2.2

ture and much larger values for the (001) surface than for the (111) one. This effect counterbalances the previous ones, and T_K for the (001) is larger than for the (111) surface.

Our results suggest that in the case of Cu, the hybridization of the Co *d* levels with the Cu *d* band is important, while in the Ag case the impurity levels should hybridize mainly with the *sp* substrate states. This can be drawn from the ϵ_d energy positions with respect to the *d* bands of the substrates, whose energy range can be extracted from the respective hybridization functions (Figs. 1 and 2).

Summarizing, we find that the main contributions to T_K come from the position of the Co impurity *d* level and from the hybridization function. The observed experimental trends are due to the competition between the structure and value of the hybridization function and the surface orientation dependence of the *d* impurity level. In the case of Cu surfaces, the impurity level hybridizes mainly with the substrate's *d* band and the hybridization function determines the values of T_K. In the case of Ag, the Co impurity levels hybridize with the *sp* states of the substrate and both orientations provide a similar hybridization. For the Ag substrates, the impurity *d* level position is the factor that determines the relative T_K values, which go in the opposite sense as for Cu. As a concluding remark it can be said that only by taking into account the correct chemical nature of the involved multiorbital problem, together with a many-body treatment, it is possible to obtain a satisfactory explanation for the measured trends in T_K.

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