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## Kondo-effect of substitutional cobalt impurities at copper surfaces

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**Abstract.** The influence of the coordination on the Kondo temperature of a magnetic impurity at a noble metal surface and the line shape observed in low temperature scanning tunneling spectroscopy (STS) is investigated for single cobalt atoms adsorbed on and embedded in copper surfaces. Surprisingly, the Kondo temperature for substitutional cobalt atoms is almost the same as that of adatoms on the Cu(100) surface. This is in stark contrast to the behaviour observed at the Cu(111) surface. DFT calculations reveal that in the case of Cu(100) the coupling of the spin of the cobalt atom to the conduction band is not substantially increased by the incorporation of the cobalt atom. At the same time the observed line shape differs strongly from what is observed on adatom systems.

The Kondo effect has attracted new interest in the past years since it has been found that it can be observed on single magnetic impurities by low temperature scanning tunneling spectroscopy (STS) [1]. It describes the screening of the spin of a magnetic impurity such as a magnetic adatom at temperatures well below the so-called Kondo temperature  $T_K$  due to an antiferromagnetic interaction between the impurity spin and the spins of the surrounding

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conduction band electrons. The formation of a many-body state leads to a sharp resonance in the local density of states (LDOS) near the Fermi energy. It is this resonance that is responsible for the peculiar macroscopic properties of dilute magnetic alloys and which can be observed as a resonance with a Fano line shape on single magnetic impurities at surfaces by STS.

A number of adatom/substrate systems have been investigated by STS and corresponding Kondo temperatures as well as line shapes have been determined [1]–[6]. More recently, also the Kondo resonance of impurities in the first monolayer has been probed experimentally for cobalt on Cu(111) [7]. In this case, it has been found that the width of the Kondo resonance of the embedded cobalt impurity increases by a factor of 8 compared to a cobalt adatom on Cu(111).

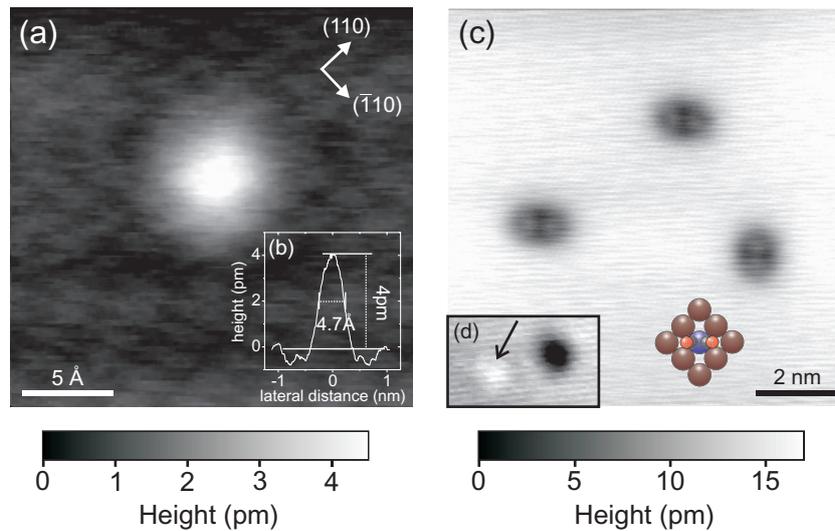
The Kondo resonance observed in tunneling spectroscopy of magnetic adatoms on metal surfaces usually does not show up as a peak in the spectrum as one might expect from theory but rather as a dip. Peaks for the Kondo state of surface systems have been observed either in molecular complexes [8] or on adatoms decoupled from the metal surface [9]. Theoretically, the line shape observed in STS has been interpreted either by interfering tunneling channels—a direct one into the localized orbital of the impurity and an indirect one to the conduction band of the host [4, 10]—or in models which propose that the line shapes observed can be understood by taking into account only tunneling into the conduction band of the substrate [11]–[14].

In this paper, we present measurements on single cobalt atoms at substitutional sites in the first monolayer of the Cu(100) substrate. We find a surprisingly low Kondo temperature similar to that of adatoms on Cu(100), while the line shape is different—showing a strong peak in the tunneling spectrum rather than a dip. An explanation for the magnitude of the Kondo temperature is offered based on an evaluation of the hybridization between the cobalt d-orbital and the conduction band of the substrate from density functional theory (DFT) calculations.

Experiments have been performed on a Cu(100) single crystal, prepared by sputtering and annealing cycles in ultra high vacuum (UHV) (base pressure  $1 \times 10^{-10}$  mbar). After cleaning the sample, minute amounts of cobalt have been evaporated from a cobalt rod in a commercial electron beam evaporator. Typical coverages were of the order of 0.001 ML. During evaporation, the sample was held at a temperature of  $\sim 320$  K. At this temperature, exchange processes between cobalt adatoms and copper atoms in the first monolayer are activated [15, 16]. After preparation, the sample was transferred *in situ* into a home-built UHV-STM operating at 6 K. Spectroscopic measurements were performed with open feedback loop using a lock-in technique with a modulation of the bias voltage of 1.5–3 mV<sub>RMS</sub> at a frequency of 4.5 kHz. The bias voltage is applied to the sample, energies given in this paper are with respect to the Fermi level. Analysis of the tunneling spectra has been performed on background subtracted spectra to remove tip-related structures except where explicitly stated. To this end a spectrum taken with the same tip on the clean Cu(100)-surface is subtracted from the spectrum taken on the impurity with the same tunneling parameters before opening the feedback loop [18], without further normalization of spectra.

We have performed DFT calculations [19]<sup>6</sup> employing the generalized gradient approximation (GGA) by Perdew *et al* [20] as the exchange-correlation function in the Kohn–Sham equations. The surface was modeled by a slab consisting of seven layers of

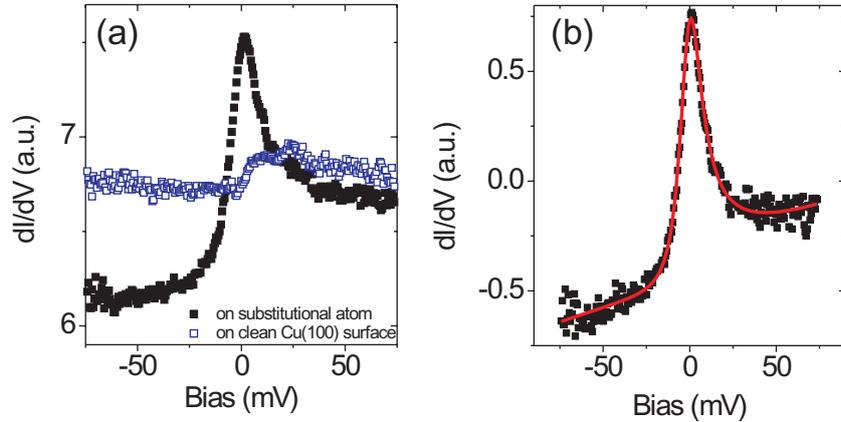
<sup>6</sup> In particular, we used the VASP code and projector augmented-wave (PAW) method with a plane wave basis set up to 25.1 Ry for the wave functions and 38 Ry for the augmentation of the charge density. We accounted for the different asymptotic potentials from the two surfaces with an opposing dipole layer and the surfaces of the slab were separated by a vacuum of 16 Å.



**Figure 1.** (a) Single cobalt impurity embedded in the 1st monolayer of the Cu(100) substrate. Image taken at  $U = 78$  mV,  $I = 1$  nA. (b) Line cut through the impurity in (a). (c) Topography of three embedded cobalt atoms with two CO molecules attached to each of them to mark them ( $U = -0.3$  V,  $I = 1.8$  nA). The ball model shows the structure of the substitutional cobalt atom (blue) and the CO molecules. (d) After removal of the CO molecules, only the cobalt atom remains at the position of the complex (left, marked by an arrow), typically one CO molecule is found on the surface in the vicinity of the cobalt impurity (imaged as a depression, the CO molecule can be identified by its spectroscopic signature due to vibrational excitations [17]).

substrate, with the cobalt atom adsorbed only on one side of the slab either on top of the surface layer or within the first layer of the slab. We allowed the three top-most layers to relax and passivated the opposite side of the slab with hydrogen at the hollow sites. The lateral dimension of the surface was  $4 \times 4$  atoms. A  $(4 \times 4)$  grid of Monkhorst–Pack k-points in the first Brillouin zone was used to approximate the integration over the reciprocal space during the atomic relaxation, and a  $(20 \times 20)$  grid was used for the analysis of the projected density of states. The occupation numbers of the Kohn–Sham states were broadened by a Fermi–Dirac distribution with a width of 50 meV.

After transfer to the STM, single cobalt impurities at substitutional sites of the copper substrate can be found (see figure 1(a)). They are imaged with an apparent height of  $\sim 4$  pm and a full width at half maximum of  $\sim 5$  Å (see figure 1(b)); for comparison cobalt adatoms on Cu(100) are typically imaged with a height of the order of 100 pm. To check the chemical nature of the impurities, we have performed a CO titration experiment in a similar fashion to that of [16]. After deposition of cobalt as above, we have dosed 1 Langmuir CO at a sample temperature of 190 K and subsequently annealed the sample to 260 K. Above a temperature of  $\approx 200$  K, CO desorbs from the Cu(100) surface [21] while CO molecules attached to cobalt impurities remain on the surface and can thus be used as markers. Figure 1(c) shows three such complexes consisting of a substitutional cobalt impurity and adsorbed CO molecules. The complexes have a twofold symmetry which suggests a stoichiometry of 1 : 2. The  $\text{Co}_{\text{sub}}(\text{CO})_2$ -complexes (the index ‘sub’ stands for substitutional) occur in two orientations on the surface



**Figure 2.** (a) Raw tunneling spectra acquired on a single cobalt impurity and on the clean Cu(100) surface. The narrow Kondo resonance at the Fermi energy is clearly visible. (b) Same spectrum as in (a) after subtracting the spectrum of the clean surface, the solid line shows the fit of a Fano function with a linear background (equation (1)) to the data.

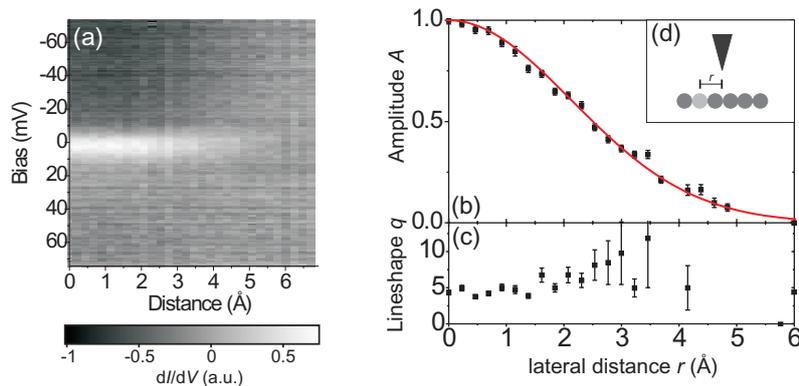
which is due to the fourfold symmetry of the Cu(100)-substrate. The CO molecules point towards the nearest hollow sites as indicated in the model in figure 1(c). By injecting electrons with a bias voltage of  $\sim 5$  V into the complexes, they can be dissociated leaving the cobalt impurity at the place of the complex as previously done for cobalt carbonyl complexes, where the cobalt atoms were on the surface instead of being substitutional impurities in the surface [8, 22]. Typically, after dissociation, one of the CO molecules can be found next to the impurity as shown in figure 1(d).

Spectroscopy on single cobalt impurities shows a narrow resonance at the Fermi level. Figure 2(a) shows spectra acquired on a substitutional cobalt atom and on the clean surface, while figure 2(b) shows the background subtracted spectrum. The resonance in the raw data has an amplitude of 20% compared to the background. It can be well described by a Fano function [11, 23] plus a linear and a constant term to account for the background,

$$\frac{dI}{dV} = a \frac{(q + \tilde{\epsilon})^2}{1 + \tilde{\epsilon}^2} + b \cdot \omega + c, \quad (1)$$

where  $\tilde{\epsilon} = \frac{\omega - \epsilon_K}{\Gamma}$  and  $\omega = e \cdot V$ .  $\Gamma$  is the half-width of the resonance,  $\epsilon_K$  its position.  $a$  is a proportionality constant. The line shape is described by  $q$  and can vary between a dip for  $q = 0$ , an asymmetric feature for  $q \sim 1$  and a peak for  $q \rightarrow \infty$ . The fit is shown in figure 2(b). We obtain the line shape parameter to be  $q = 6.5 \pm 1.9$ —describing an asymmetric peak. It has a width of  $\Gamma = 7.5 \pm 0.5$  meV which corresponds to a Kondo temperature  $T_K \approx \Gamma/k_B = 87 \pm 6$  K, the position is  $\epsilon_K = -0.5 \pm 0.5$  mV (function fitted to the full range of the spectrum as shown in figure 2(b))<sup>7</sup>.

<sup>7</sup> We have tested the influence of other normalizations of spectra applied prior to subtraction and deconvolution of spectra as described in [18] on the extracted parameters: the extracted width scatters by as much as 5% around the mean for a pair of spectra taken on the cobalt atom and on the clean surface, the variation of the line shape parameter is up to 15% as it sensitively depends on details of the background. The extracted position of the resonance stayed between  $-1$  and  $0.4$  mV for all pairs considered, where the scattering for a single pair was less than  $0.25$  mV around the mean.

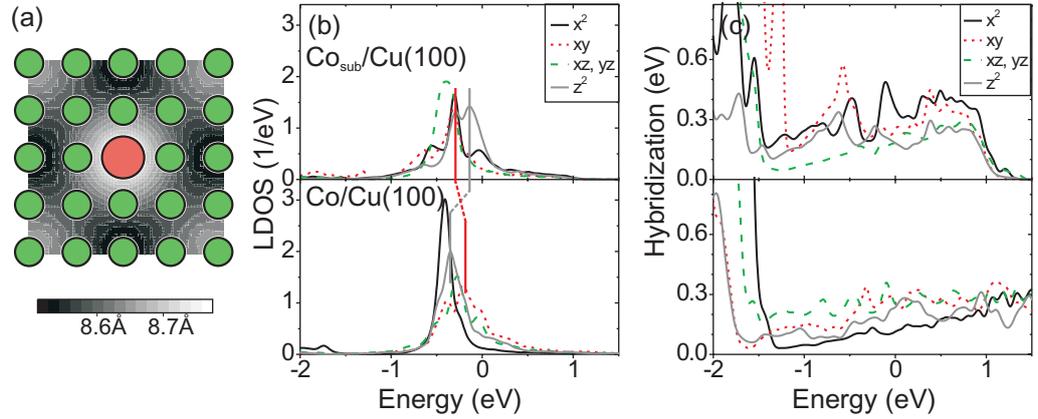


**Figure 3.** (a) Distance dependence of the Fano peak detected in tunneling spectra along a line in the (010) direction (raw data shown). (b + c) Parameters of fits of fano line shapes (equation (1)) to the background subtracted spectra, shown is (b) the amplitude  $A = a(1 + q^2)$  normalized to 1 on top of the atom (variables as in equation (1), the red line is shown as a guide to the eye) and (c) the line shape parameter  $q$ . Error bars are extracted from the covariance matrices of the fits. (d) shows a sketch of the measurement geometry.

The observed line shape close to a peak is in contrast to the spectra measured on adatoms in direct contact with metal surfaces, where values of  $q$  ranging between 0 and 1 corresponding to dips or asymmetric resonances have been reported [1], [3]–[6]. On moving the tip laterally away from the substitutional cobalt atom, a reduction in the amplitude is observed (consistent with previous work on adatoms) [5]. Figure 3(a) shows the distance dependence of the spectrum in a gray scale map, while (b) and (c) show the distance dependence of the fit parameters of equation (1). The peak as found on the atom (left border of the map) is reduced in amplitude upon moving the tip away; however, the line shape stays basically the same. Beyond 2.5 Å, the determination of the line shape becomes unreliable because the amplitude of the resonance is already substantially diminished.

The Kondo temperature (or width of the resonance) is surprisingly low in view of the high coordination of a substitutional atom and also compared to experiments on substitutional cobalt atoms on Cu(111) reported by Quaas *et al* [7]. Reasons for this can be the role of relaxation in the interaction between the d-orbital of the cobalt atom and the conduction band electrons as well as the influence of the symmetry of the adsorption site on the hybridization. A similar non-monotonicity of the Kondo temperature with the coordination has been observed previously in artificially assembled  $\text{CoCu}_n$  clusters on a Cu(111) surface [24].

To elucidate this point, we have performed *ab initio* DFT calculations for cobalt adatoms at copper surfaces, Co on and in both Cu(100) and Cu(111), to estimate the hybridization of the d-orbital with the conduction band electrons. Figure 4(a) shows a simulated STM image for the Co atom embedded in the first monolayer of Cu(100). In agreement with the experiment, the cobalt atom is imaged as a protrusion. The calculated electronic structure (obtained with  $20 \times 20$   $k$ -points in the first Brillouin zone) is analyzed to extract information on the hybridization of the d-orbitals of cobalt with their surroundings. From the projected density of states (PDOS)  $\rho_\nu$  as obtained from DFT calculations we have estimated the hybridization  $\Delta_\nu$



**Figure 4.** (a) Simulated STM image of a substitutional cobalt atom in the top-most monolayer of a Cu(100) surface with the relaxed geometry, (b) LDOS as obtained from the DFT calculations for a substitutional cobalt atom (upper graph) and a cobalt adatom (lower graph) broadened by a lorentzian with 0.1 eV width. Vertical lines indicate the position and shift of the two orbitals relevant to the adatom and substitutional atom system, (c) hybridization  $\Delta$  as calculated from equation (2) for substitutional atom and adatom.

between an orbital  $\nu$  of the cobalt atom and the substrate following Gunnarsson *et al* [25] by a Kramers–Kronig relation

$$\Delta_{\nu}(\epsilon) = -\Im \left( \int_{-\infty}^{\infty} d\epsilon' \frac{\rho_{\nu}(\epsilon')}{\epsilon - \epsilon' - i0} \right)^{-1}. \quad (2)$$

Thus, we are able to assess the hybridization for cobalt atoms on copper surfaces. In the analysis of the hybridization, we assume that the orbital which according to the DFT calculation is closest to the Fermi energy will dominate the Kondo effect of the adatom. The same analysis has been performed on the PDOS after broadening it with different widths (0.02, 0.05, 0.1 and 0.2 eV) to verify that the results stay consistent. Except for substitutional cobalt impurities in Cu(111), the analysis resulted in one orbital which was closest to the Fermi energy for all broadenings, with the next orbital being at least 25 meV away.

The results for Cu(100) are plotted in figure 4(b + c): figure 4(b) shows the PDOS for the d-orbitals of a substitutional cobalt atom and an adatom and (c) the corresponding hybridization as obtained from equation (2). It becomes apparent that the orbital which is closest to the Fermi energy changes: for the cobalt adatom, the  $d_{xy}$  orbital is closest to the Fermi level, while for a substitutional atom, the  $d_{z^2}$ -orbital moves to the Fermi level and becomes the one closest to  $E_F$ . At the same time, the hybridization of the  $d_{z^2}$  orbital for the substitutional atom which we obtain from equation (2) is smaller than for the  $d_{xy}$ -orbital of the adatom. Thus, the behavior of the Kondo temperature can be rationalized by the change in the orbital which dominates the Kondo effect and the overall reduced hybridization of the orbital closest to the Fermi energy in the substitutional atom as compared to the adatom. The results for cobalt adatoms and substitutional atoms on copper (111) and (100) are summarized in table 1. The reduced hybridization for the substitutional cobalt atom on Cu(100) can partially be attributed to the different relaxation of an adatom compared to a substitutional atom: as obtained from DFT

**Table 1.** Experimental data for the Kondo temperature  $T_K = \Gamma/k_B$  (in K) of cobalt impurities on copper surfaces. In addition, the results from the DFT calculation are shown (nearest-neighbor distance  $a$  for the impurity atom, height  $h$  above or below (negative) the topmost surface layer, name of the d-orbital(s) closest to the Fermi energy, degeneracy  $N$ , energy  $E_d$ , hybridization  $\Delta$  as extracted from equation (2)). For substitutional cobalt impurities in Cu(111), values for the two orbitals closest to the Fermi energy are given. Kondo temperatures for Co/Cu(111) and Co/Cu(100) are taken from [5], for Co in Cu(111) from [7].

System	$T_K$ (K)	$a$ (Å)	$h$ (Å)	Orbital	$N$	$E_d$ (eV)	$\Delta$ (eV)
Co/Cu(111)	$54 \pm 3$	2.35	1.73	xy, $x^2$	4	-0.22	0.13
Co in Cu(111)	$405 \pm 35$	2.55	-0.14	xy, $x^2$	4	-0.32	0.31
				$z^2$	2	-0.33	0.22
Co/Cu(100)	$88 \pm 4$	2.35	1.46	xy	2	-0.21	0.24
Co in Cu(100)	$87 \pm 6$	2.54	-0.06	$z^2$	2	-0.14	0.22

calculations here and previously by Pentcheva and Scheffler [26], adatoms are relaxed towards the surface by roughly 16%, whereas substitutional impurities relax only by about 7%. The higher coordination of the substitutional cobalt atom compared to an adatom on either Cu(111) or (100) would suggest that the hybridization with the substrate should be higher and hence the Kondo temperature of a substitutional impurity be larger than that of an adatom [5]. However, this is not the case for a cobalt atom on Cu(100) as can be seen from table 1. Hence, the behavior cannot be understood by only considering the number of nearest neighbours, in addition at least the relaxation has also to be taken into account. Furthermore a change in the partially occupied orbital which supposedly dominates the Kondo effect is observed in DFT calculations. The situation is different for Cu(111), where a similar analysis for adatoms and substitutional atoms shows that the hybridization with the conduction band rises with the coordination thus leading to an increase in the Kondo temperature as found by Quaas *et al* [7]. In agreement with the calculations by Barral *et al* [27], for the adatom on Cu(111) the hybridization is found strongest for the  $d_{z^2}$ -,  $d_{xy}$ - and  $d_{yz}$ -orbitals; however, from the energies of the orbitals, the  $d_{xy}$ - and  $d_{x^2}$ -orbitals are closest to the Fermi energy and hence, we assume them to dominate the Kondo effect. Concerning the line shape of the substitutional atom on Cu(100), the orbital which from the DFT analysis is nearest to the Fermi energy changes towards the  $d_z^2$ -orbital for the substitutional impurity. The change in line shape would be consistent with the idea that the coupling of the  $d_z^2$ -orbital to the tip is larger than for the  $d_{xy}$ -orbital in the case of an adatom; however, we have no evidence of a dependence of the line shape on the lateral distance between the tip and the cobalt atom as one would expect for substantial coupling between tip and d-orbital of the impurity [5, 10]. Similar line shapes with a large value of  $q$  as for the substitutional impurity on Cu(100) have been observed previously where the impurity was embedded in a molecular complex [8] and recently for a cobalt atom on CuN on Cu(100) [9]. In the latter case, it was also stated that there was no significant dependence on the vertical distance between the tip and the cobalt atom, in contrast to what would be expected for a substantial contribution of a direct tunneling channel [10]. Neither have we observed oscillations in the line shape with the Fermi wave vector  $k_F$  of the substrate as can be seen in figure 3, as was predicted

in the case of no coupling between tip and impurity orbital [11]. Our findings support models for the line shape of the Kondo resonance which neglect a direct tunneling channel [10]–[13] even in the case of comparatively large value of  $q$  as found here. The absence of oscillations in the line shape with lateral distance from the impurity can be rationalized by the tip coupling predominantly to states with  $k_{\parallel} = 0$  [12].

The potential of our analysis in estimating Kondo temperatures could be further tested for other adatom/substrate systems where experimental data on the Kondo temperature are available, which is specifically the case for cobalt atoms on noble metal surfaces. The main difficulty in comparing the analysis for other substrates or other magnetic impurities lies in estimating the Coulomb repulsion and the precise energy of the d-orbital from *ab initio* calculations, as both can substantially influence the resulting Kondo temperature.

In conclusion, we have presented measurements for substitutional cobalt impurities in the Cu(100)-surface. Spectra acquired on these impurities show a narrow peak near the Fermi level, which is interpreted as a Kondo resonance. We find that the Kondo temperature for a substitutional impurity is on the same order as for the cobalt adatom, while the line shape differs substantially from other adatom systems. Our experiments do not indicate a substantial contribution of a direct tunneling channel into the impurities d-level as might be expected for the observed peak-like line shape. The results rather support models which explain the line shape as being due to the electronic structure of the substrate [11]–[14]. Comparison with DFT calculations supports a picture where the hybridization of the orbital which dominates the Kondo effect does not increase substantially when going from an adatom to a substitutional cobalt atom on Cu(100).

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