Kondo Effect of Single Co Adatoms on Cu Surfaces

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The Kondo resonance of Co adatoms on the Cu(100) and Cu(111) surfaces has been studied by scanning tunneling spectroscopy. We demonstrate the scaling of the Kondo temperature T_K with the host electron density at the magnetic impurity. The quantitative analysis of the tunneling spectra reveals that the Kondo resonance is dominated by the Cu bulk electrons. While at the Cu(100) surface both tunneling into the hybridized localized state and into the substrate conduction band contribute to the Kondo resonance, the latter channel is found to be dominant for Cu(111).

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How localized electrons interact with delocalized electrons is a question central to many forefront problems in condensed matter physics. One of the simplest examples is the Kondo effect, which occurs when a magnetic impurity atom is placed in a metal. The Kondo effect is a correlation of the conduction band electrons of a metal host with the unpaired electrons of the magnetic impurity due to spin flip scattering processes. As the temperature of the system approaches 0 K, a many electron singlet state is formed enhancing the local density of states (LDOS) near the Fermi energy at the site of the impurity. By exploiting atomic-scale spatial resolution and meV energy resolution, scanning tunneling spectroscopy has been used to locally probe the interaction of single magnetic impurities with host metal conduction electrons. Sharp zero bias spectroscopic features of single magnetic atoms on noble metal surfaces at low temperatures were found and interpreted as a fingerprint of the Kondo resonance [1,2].

The Fano line shaped [3] tunneling spectra taken with the scanning tunneling microscope (STM) tip on top of the magnetic adatoms have been interpreted by an interference of two tunneling channels, one direct channel through the resonance localized on the magnetic impurity and another channel into the conduction band of the substrate, but questions remain about the strength of the direct channel and the spatial changes of the Fano line shapes [4,5]. Also, thus far only systems with a surface state present at the Fermi energy have been investigated [1,2,6,7], yet the role of the surface state electrons in the Kondo resonance needs to be examined.

In the present Letter, we address these questions by a comparative study of the interaction of Co adatoms with the conduction band electrons of the Cu(100) and Cu(111) surfaces. The spatially resolved scanning tunneling spectroscopy measurements of individual adatoms are quantitatively analyzed with the model of Plihal and Gadzuk [8]. In both systems, the Kondo resonance is detectable only within 10 Å of lateral tip-adatom distance r, signifying an inferior role of the Cu(111) surface state in the formation of the Kondo resonance. The r dependence of the line shape and amplitude of the tunneling spectra reveals that direct tunneling into the localized state is negligible for Cu(111) but important for Cu(100). We also demonstrate the correlation of the Kondo temperature T_K with the host electron density at the magnetic impurity.

We have analyzed the size and the shape of the Kondo resonance at and in the vicinity of isolated Co adatoms on the Cu(100) and the Cu(111) surfaces by means of low temperature ($T = 6$ K) scanning tunneling spectroscopy. The single crystal Cu(100) and Cu(111) substrates have been cleaned in ultrahigh vacuum by repeated cycles of annealing and Ar^+ ion sputtering. About 10^{-3} monolayer of Co were evaporated onto the cold substrates from a thoroughly degassed Co (99.996%) wire wound around a 99.95% W filament, whereon the surfaces were covered with isolated immobile Co adatoms (Fig. 1). Differential conductance $dI/dV(V)$ spectra are taken by stabilizing the tip at the adjusted tunneling resistance, opening the feedback loop, and ramping the voltage. The dI/dV signal is obtained using a lock-in technique with a 4 kHz voltage modulation of $\sim$1 mV rms. All voltages are sample potentials measured with respect to the tip. We have used an STM tip chemically etched from a pure tungsten wire and cleaned by field emission (300 μA, 600 V). The tip apex wave function was modified by dipping the tip into the substrate ($\sim$1 nm) until the adatoms are imaged spherically and the $dI/dV(V)$ spectra on the bare surface have no sharp features near zero bias. This way, the tip apex wave function is symmetric and optimized for spectroscopy at the expense of high spatial resolution (i.e., minimizing the radius of the tip apex wave function). Tips prepared in this way reproducibly image the Co adatoms as bumps in the constant current images $\sim$1.1 and $\sim$0.8 Å high with a diameter (FWHM) of $\sim$8 and $\sim$6 Å for Co on Cu(100) and Cu(111), respectively (Fig. 1).

We find Co on Cu(100) and Cu(111) to be Kondo systems characterized by Fano-type scanning tunneling spectra near E_F (Fig. 2). We analyze the spectra in the framework of two competing tunneling channels: For $T \ll T_K$, where spin flip processes are frozen, local Fermi liquid theory can be applied and the Kondo resonance in the LDOS of the d level has a Lorentzian shape [5,10]. Tunneling into this LDOS, which is hardly accessible due to the strong localization of the $3d$ orbital at the atomic

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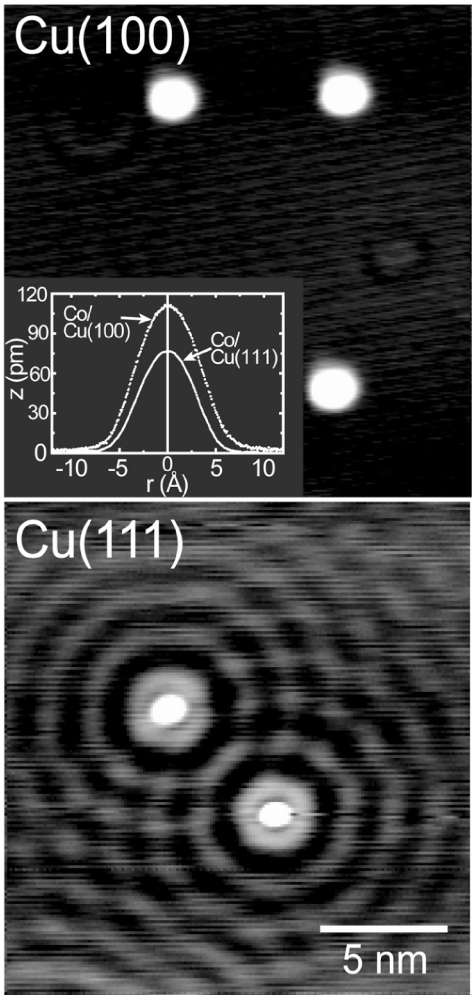

FIG. 1. Constant current STM images (−50 mV bias, I = 2 nA) of Co adatoms on the Cu(100) (three atoms) and the Cu(111) surface (two atoms). The Friedel oscillations of the Cu(111) surface state electrons can be easily detected up to 10 nm. The inset compares line cuts in the z signal over the adatoms on the two different surfaces for typical tip conditions.

core, makes up only one part of the tunneling current; the other part is from tunneling into the conduction electron LDOS of the substrate modified by the presence of the Kondo impurity. These two tunneling channels interfere and the resulting tunneling LDOS, which is proportional to the measured dI/dV signal, has a Fano line shape. In contrast to the atomic excitation spectra studied by Fano, the tunneling line shape is not fixed but varies with the lateral tip-adatom distance r. We describe the tunneling conductance close to zero bias as

$$dI/dV(r,V) = c + a(r)\,\frac{q(r)^2 - 1 + 2q(r)\epsilon}{\epsilon^2 + 1}, \quad (1)$$

with $\epsilon = (eV + \Delta E)/k_B T_K$. Here, c is the background dI/dV signal, and ΔE is a small shift of the resonance from the Fermi energy due to level repulsion between the d level and the Kondo resonance. The Fano line shape

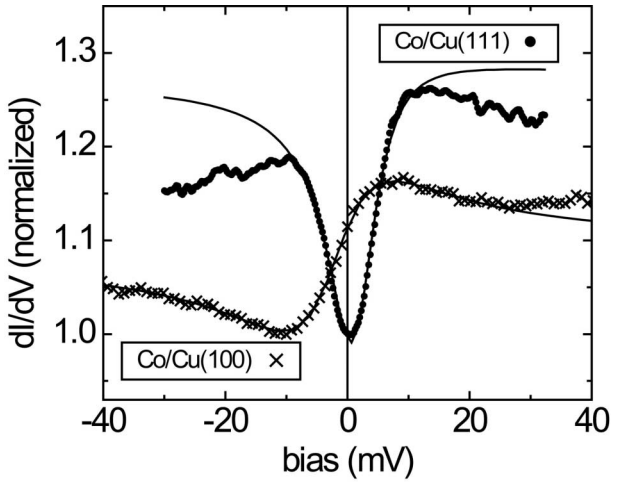

FIG. 2. Atom differential conductance (dI/dV) spectra for Co/Cu(100) and Co/Cu(111). The tunneling resistance was 10 MΩ. The spectra are normalized to their lowest values. The solid lines are Fano line shape fits according to Eq. (1); average parameters are summarized in Table I.

parameter q is given by [5,8]

$$q(r) = \frac{\mathrm{Re}G(r) + t(r)}{\mathrm{Im}G(r)}, \quad (2)$$

with $G(r)$ a modified conduction electron Green's function as seen by the tip, and t is a function proportional to the matrix element for direct tunneling into the localized state. $t(r)$ depends on the overlap of the tip wave function with this state and will fall off rapidly with r. It is modeled as $t(r) = t_0 \exp[-d(r)/\alpha]$, with a decay length α and the overall tip-adatom distance $d(r)$ (see inset of Fig. 3). With q defined as in Eq. (2), $a(r)$ is proportional to $[\mathrm{Im}G(r)]^2$. The Fano line shape is a negative Lorentzian for $q = 0$, a positive Lorentzian for $q = \pm\infty$, and most asymmetric for $q = \pm 1$. Even for $t = 0$, i.e., no direct tunneling into the localized state, any Fano line shape can result due to the first part of q, $\mathrm{Re}G/\mathrm{Im}G$, which describes an indirect tunneling from the tip to the adsorbate by conduction electron propagation. This first part gives rise to rapid oscillations of q between asymmetric Fano and symmetric Lorentzian line shapes with a period of π/k_F ($\pi/k_F^b = 2.6$ Å for the free bulk electrons) [4,5]. But, as we will see below, these oscillations are not resolved by

TABLE I. Mean Fano line shape parameters and Kondo temperatures T_K from fits of Eq. (1) to scanning tunneling spectra of ten different Co adatoms on Cu(100) and Cu(111). n is the number of nearest neighbor Cu atoms.

	Co/Cu(111)	Co/Cu(100)	Co in bulk
T_K [K]	54 ± 2 53 ± 5 [6]	88 ± 4	~500 [9]
n	3	4	12
q	0.18 ± 0.03	1.13 ± 0.06	
ΔE [meV]	1.8 ± 0.6	−1.3 ± 0.4	

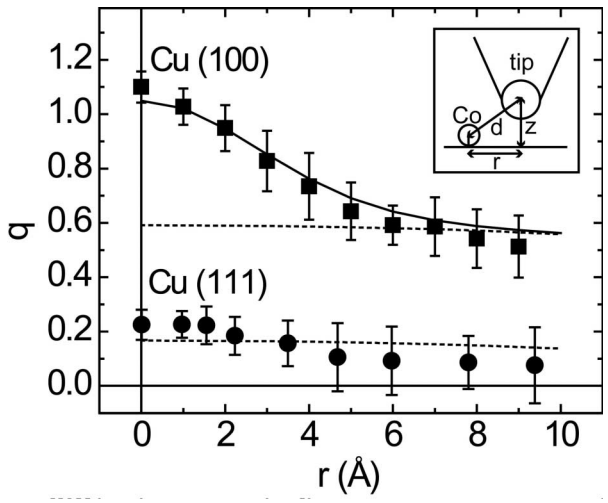

FIG. 3. Spatial dependence of the Fano line shape parameter q on the in-plane tip-adatom distance r for Co/Cu(100) and Co/Cu(111). Each data set presents averaged values from measurements on four atoms. The dotted lines are from calculations with no direct tunneling into the localized state, for the solid line $t(r)$ was fitted as described in the text. The inset shows the measurement geometry.

the STM in the usual spectroscopic tunneling conditions with the tip about $5 < z < 10$ Å above the surface. By modeling the host metal electrons with a jellium model [8], the oscillations in G are found to be lost for $z > 5$ Å. We further define the overall amplitude A of Eq. (1) as the distance from the lower minimum to the upper maximum:

$$A(r) = a(r)[1 + q(r)^2]. \tag{3}$$

We fitted Eq. (1) to on-atom ($r = 0$) $dI/dV(V)$ curves taken on different adatoms and with different tip structures. Prior to fitting, the $dI/dV(V)$ curves are normalized to their minimal value. The form of the spectra did not change for different tunneling resistances in the range of 0.2 to 100 MΩ. Average Fano line shape parameters from fitting ten different on-atom differential conductance spectra for Co on Cu(100) and Cu(111) are summarized in Table I. We determine Kondo temperatures of $T_K = (88 \pm 4)$ and (54 ± 2) K for Co on the Cu(100) and Cu(111) surface, respectively. The Cu(111) value is in very good agreement with the T_K value of (53 ± 5) K reported by Manoharan *et al.* [6].

The Kondo problem is essentially determined by only one relevant energy scale, $k_B T_K$. Once the Kondo temperature is known, predictions for all relevant physical observables can be made. The Kondo temperature itself should depend only on the strength of the exchange coupling J and the density of the conduction electron states ρ at the magnetic impurity [10]:

$$T_K = T_0 e^{-1/(2J\rho)}. \tag{4}$$

The increase in T_K from Cu(111) to Cu(100) to bulk Cu (see Table I) is due to an increase in $J\rho$ which is in turn related to an increase of the number of nearest neighbor Cu atoms n. From atomic resolution images for Co/Cu(100), we determined the Co adatom site to be the fourfold hollow site ($n = 4$); for Co/Cu(111), the adsorption site is known to be the threefold hollow site [11], i.e., $n = 3$. We find that the logarithm of the Kondo temperature falls off linear with $1/n$. A fit of T_K to Eq. (4) with $J\rho \sim n$ yields $T_0 = 10^{3.00\pm0.12}$ K and $J\rho = (0.055 \pm 0.007)n$.

We now turn to the influence of the surface state electrons on the Kondo resonance. To this end, we have investigated the change of the Fano resonances with the in-plane tip-adatom distance r by scanning over the adatoms and taking tunneling spectra for different r. $q(r)$ and $A(r)$, as determined from fits of Eq. (1) to spectra taken on four different Co adatoms on Cu(111) and Cu(100), are shown in Figs. 3 and 4. The errors are due to different tip structures, variations for different adatoms, and noise in the dI/dV signal for larger r. For both systems the Kondo spectra are detectable only for $r < 10$ Å (Fig. 4). The similar decay of $A(r)$ clearly indicates that the Cu(111) surface state does not significantly contribute to the formation of the Kondo resonance: Because of its two dimensional character, $A(r)$ for the surface state electrons should fall off only with $1/r$, whereas $A(r)$ for the bulk electrons falls off as $1/r^2$ [8]. On the bare Cu(111) surface, about 2/3 of the current tunnels into the surface state. This can be seen from the corresponding increase of the dI/dV signal at the onset (−440 mV) of the surface state [12]. But it is known that, close to strongly bound adsorbates, the tunneling channel into the surface state is lost: The surface state onset can no longer be detected on the adsorbate, and the adsorbate Friedel oscillations of the surface state are those of a highly absorbing (black dot) scatterer [13–15]. The surface state electrons thus scatter into bulk states at the Co adatoms which can explain why their share in the Kondo resonance is below the experimental resolution. That they are not entirely uninvolved was demonstrated by Manoharan *et al.* [6,14] in an ellipse corral experiment, where a Fano spectrum was found in one focus about 8 nm away from the

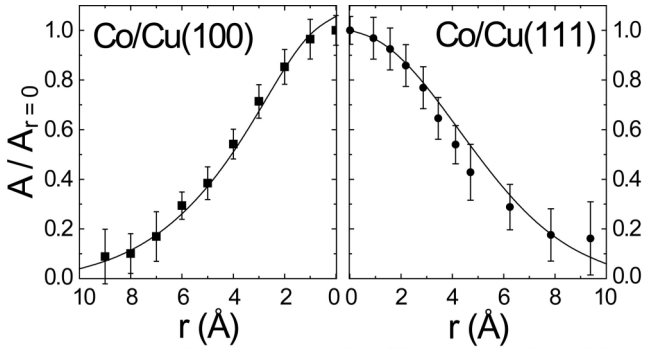

FIG. 4. Spatial dependence of the normalized amplitude of the Fano resonance $A(r)/A(0)$ on the in-plane tip-adatom distance r for Co/Cu(100) and Co/Cu(111). Each data set presents averaged values from measurements on four atoms. The solid lines are from model calculations described in the text.

Co adatom in the other focus. In agreement with our finding of a weak surface state contribution to the Kondo resonance, the spectrum in the empty focus was strongly diminished and detectable only for ellipse corrals formed in a way that the Fermi energy surface state density at the adatom is enhanced.

Whereas $q(r)$ for Co/Cu(111) keeps its small on-atom value $q(0)$ within the error, $q(r)$ for Co/Cu(100) falls off strongly within $r < 6$ Å (Fig. 3). In both systems, no oscillations in $q(r)$ are observed as expected for tip distances $z > 5$ Å [8]. Accordingly, the difference in the spatial behavior of the asymmetry in the Fano line shape can be ascribed to substantial differences in the relative weight of the two competing tunneling channels for the two surfaces. In order to analyze the contribution of the tunneling channels into the resonance localized on the Co adatom and into the Cu substrate states quantitatively, we model $A(r)$ and $q(r)$ with a jellium model for $G(r)$ under consideration of the tip-surface distance z according to a recent model by Plihal and Gadzuk [8]. This is done by first fitting $[\mathrm{Im}G(r)]^2$ to the measured $a(r)$. Then, $\mathrm{Re}G(r) + t(r)$ is fitted to $\mathrm{Im}G(r)$ times the measured $q(r)$ [see Eq. (2)]. In the case of Co/Cu(111), this can be done with $t(r) = 0$. In contrast, in the case of Co/Cu(100), the direct channel $t(r)$ has to be considered to describe the measured $q(r)$. We find, with the decay constant $\alpha = 0.75$ Å [8], $t_0 = 170$ and $z = 9.1$ Å. The calculated $q(r)$, with and without the direct tunneling channel, are shown in Fig. 3. Finally, $A(r)$ as calculated according to Eq. (3) with the $\mathrm{Im}G(r)$, $\mathrm{Re}G(r)$, and $t(r)$ obtained above nicely follows the experimental data for both systems (Fig. 4).

In conclusion, we find Co/Cu(100) to be a Kondo system of $T_K = 88$ K. This increased T_K compared to $T_K = 54$ K for Co/Cu(111) can be explained by a higher bulk electron density at the adatom. The asymmetry of the on-atom Co/Cu(100) Fano line shape is partly due to direct tunneling into the localized state as concluded from the decay of $q(r)$ within $r < 6$ Å. In contrast, the almost symmetric Co/Cu(111) Fano line shape can be ascribed to the dominance of the tunneling into the substrate conduction band. For both systems, the Kondo resonance is detectable only close to the adatoms for $r < 10$ Å, indicating that the electrons of the Cu(111) surface state play only a minor role in forming the Kondo resonance. Form and spread of $A(r)$ and the nonoscillating character of $q(r)$ can be reproduced with a jellium model for the conduction band taking the finite z into account.

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