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Kondo state of Co impurities at noble metal surfaces

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ABSTRACT We use scanning tunneling microscopy and spectroscopy to study the properties of magnetic Co adatoms on noble metal surfaces at 6 K. Due to spin-flip scattering of the substrate electrons at the impurity the many-body Kondo state forms. This state is characterized by an energy, the Kondo temperature T_K . We measure T_K of adatom systems and a resonant scattering phase shift locally and are thus able to discuss the coupling of the Co adatom to the metal electronic system. From the resonant scattering phase shift of the surface-state electrons scattering off a Co adatom on Ag(111), we find that the coupling to the surface state is rather weak. On the other hand, increasing the number of nearest neighbor substrate atoms increases the coupling of a Co adatom to the host metal and increases T_K . This shows the dominant character of the coupling of the Co atom to the bulk states of the substrate crystal.

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1 Introduction

The interaction of a magnetic impurity with the electrons of a non-magnetic host serves as a paradigm of many-body physics [1]. Interest into the classical Kondo effect has been renewed when it was shown that the properties of Kondo systems consisting of magnetic adatoms on metal surfaces can be studied by scanning tunneling microscopy (STM) [2, 3]. The Kondo state is formed by the interaction of the electronic spin on the adatom with the electron sea of the host metal. This interaction leads to a many-electron ground state where the host electrons screen the spin of the impurity [1]. The Kondo temperature T_K can be thought of as the binding energy of the correlated state (0..1000 K) and can be directly measured by low temperature scanning tunneling spectroscopy (STS). Provided that the temperature of the experiment T is low compared to T_K (as is the case for the results reported here) a resonance of width $2k_B T_K$ is formed in the density of states of the impurity atom at the Fermi energy E_F . This resonance shows up in the differential conductance of the tunneling contact dI/dV at the lateral adatom position (the STM tip being 5–10 Å away from the surface) as a Fano

resonance [2–5]. A number of different adsorbate-substrate systems have been investigated by now [6–14], but there is only little progress in understanding theoretically which states contribute to the formation of the Kondo system and how the relative magnitudes of the Kondo temperatures can at least semi-quantitatively be understood [15, 16].

We present here results obtained by low temperature STM and STS concentrating on understanding which states at the metal surface play a major role in forming the Kondo ground state and how trends of the Kondo temperature can be understood when comparing different adsorption geometries of the adsorbate on a specific host material. In Sect. 3 we study the interaction of the surface-state electrons with the magnetic impurity by measuring the scattering phase shift. In Sect. 4 we discuss the behavior of T_K when the number of nearest neighbors around the adatom is changed.

2 Experimental

Single crystal surfaces were prepared by standard sputtering and annealing cycles in ultra-high vacuum (base pressure 1×10^{-10} mbar). The samples were then transferred in situ to an STM working at 6 K. Co adatoms were produced by dosing Co from a carefully out-gassed tungsten wire with a Co wire of 99.99% purity wrapped around it. During that process the sample temperature stayed below 20 K ensuring the formation of single adatoms due to a repulsive interaction between them on noble metal (111) surfaces [17]. Spectroscopic measurements were performed using a lock-in technique with a modulation of the sample voltage of 1 mV_{RMS} at a frequency of 4.5 kHz. All bias voltages are sample potentials measured with respect to the tip.

3 Kondo effect and resonant scattering: interaction with surface-state electrons

The first STS experiments with Kondo impurities were all carried out on noble metal (111) surfaces. These surfaces exhibit a surface state at E_F situated inside a band gap occurring in the [111] direction of the bulk crystal. The surface states are very attractive for investigations by STM since they are to some degree decoupled from the bulk states and have considerable amplitude at the tip position in vacuum above the surface. Furthermore, the surface-state electron density can be modified laterally by defects like steps or

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adatoms. Manoharan et al. studied the behaviour of an atom-by-atom assembled elliptical resonator on Cu(111) where a Co adatom was put into one of the foci. They found a Kondo resonance not only on the adatom but also some 70 Å away in the empty focus [7]. The resonator confined the surface-state electrons and many theoretical treatments looked at the consequences of the interaction of a surface magnetic impurity with a two-dimensional electron gas [18–21]. Obviously, there is some interaction with the surface state, otherwise the “quantum mirage” [7] would not work. At the heart of the theoretical examination is the idea that the mirage is due to a special phase-shift the scattering electrons acquire when scattering off the impurity [18]. According to Nozières a Kondo impurity that is spin-screened in its ground state acts like a potential scatterer with a resonant level at the Fermi energy [22]. Electrons scattering off the impurity acquire an energy dependent phase shift which increases by π when crossing the resonance energy. Such a scattering phase shift can of course be sensed in the far field of the scatterer, as long as the electrons keep their phase coherence [23]. The existence of an interaction between surface-state electrons and the magnetic impurity does not automatically mean that surface-state properties determine the Kondo temperature or the line shape of the Kondo resonance STS spectrum. The latter is – at least for Co on Ag(111) – not the case, as we will demonstrate in the following.

In Fig. 1 we show the results obtained by STM and STS on a Co impurity on Ag(111). In the topograph (Fig. 1a) the Co adatoms are imaged as protusions for all practical tunneling voltages (± 1 V, at higher voltages the adatoms tend to be moved by the STM tip). There are also defects imaged as depressions, these are non-magnetic adsorbates or impurities that are situated in the first surface layer. The dI/dV spectrum on the Co adatom shows in the case of Co on Ag(111) an anti-resonance (Fig. 1b). In general the line shape is a Fano resonance [2–5] given by:

$$\frac{dI}{dV} \propto \frac{(q + \varepsilon)^2}{1 + \varepsilon^2} \quad (1)$$

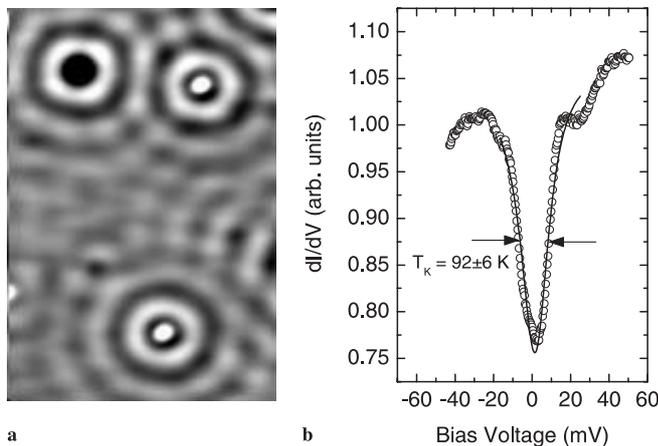


FIGURE 1 (a) (40 nm \times 50 nm) STM-topography of 2 Co adatoms and a surface layer impurity on Ag(111). The defects are surrounded by interference patterns caused by electron scattering. (b) dI/dV spectrum taken with the tip positioned directly on top of the adatom (open symbols). The Kondo temperature T_K is obtained from a fit of the data to (1) (solid line)

where $\varepsilon = \frac{eV - \varepsilon_K}{\Gamma}$ is the normalized energy and ε_K is the position of the resonance of width Γ relative to the Fermi energy. We identify the Kondo temperature T_K with the half width Γ/k_B of the measured resonance. For Co on Ag(111) we find an average value of $T_K = 92 \pm 6$ K [12], which has been confirmed by Limot and Berndt [24]. The intrinsic surface impurities which are imaged as depressions show no feature near the Fermi level and will therefore be used as a reference non-magnetic scatterers.

Both defects are surrounded by an interference pattern caused by the density modulation in the two-dimensional electron gas 2DEG of the surface-state electrons [25]. These local density of states (LDOS) oscillations can be understood in terms of electrons that are emitted from the tip and are scattered back with a certain phase relation [26]. Accordingly one can write the varying part of the LDOS $\Delta\varrho(r, E)$ caused by s-wave scattering as:

$$\Delta\varrho(r, E) = L_0 \left(1 - \frac{1}{4\pi} \Im \left(\frac{e^{i2\delta(E)} - 1}{2i} H_0^2(k(E)r) \right) \right) \quad (2)$$

where L_0 is the density of states for a 2DEG, $\delta(E)$ is the scattering phase shift, $k(E)$ the dispersion of the surface state, $H_0(x)$ is the zeroth-order Hankel-function, and $\Im()$ denotes the imaginary part. For $kr > 1$ the simpler formula given by Heller et al. [26] can be used. From the LDOS one obtains the tunneling current as:

$$I(r, V) \propto e^{-A\sqrt{\Phi}z} \int_0^{eV} \Delta\varrho(r, E) dE \quad (3)$$

where the constant A is $1.025 \text{ \AA}^{-1} eV^{-1/2}$. By setting $I(r, V) = \text{const.}$ (3) can be inverted to give the constant current topography $z(r, V)$.

From the experiments with the so-called “quantum corals” [25] it is known that an adatom acts predominantly as an absorptive scatterer. Therefore the adatom scattering pattern can be very well described by a purely imaginary phase shift [26]. For a Kondo impurity we combine the elastic resonant phase shift with the absorptive contribution and write the scattering phase shift as [12, 18]:

$$\delta(E) = \frac{\pi}{2} + \arctan \left(\frac{E - \varepsilon_K}{k_B T_K} \right) + \delta_{bg} + i\delta_{ab} . \quad (4)$$

The arctan term is due to the resonant scattering at the Kondo impurity. It is not present for a non-magnetic impurity for which we in the following assume an energy independent complex phase shift. For impurities at surfaces it was argued that a “background” phase shift δ_{bg} should be considered caused by other resonances near the Fermi level [18]. The last term δ_{ab} which reflects absorptive scattering is responsible for the difficulty to detect the elastic part of the phase shift in the wave pattern around an impurity (Fig. 1a) [25, 26]. To demonstrate this and to motivate the following analysis we compare in Fig. 2 the bias dependence of the wave pattern of the calculated constant current topography $z(r, V)$ around a Co adatom with that around a non-magnetic impurity. The Co adatom is characterized by an energy dependent scattering phase shift according to (4) in which we use ε_K and T_K

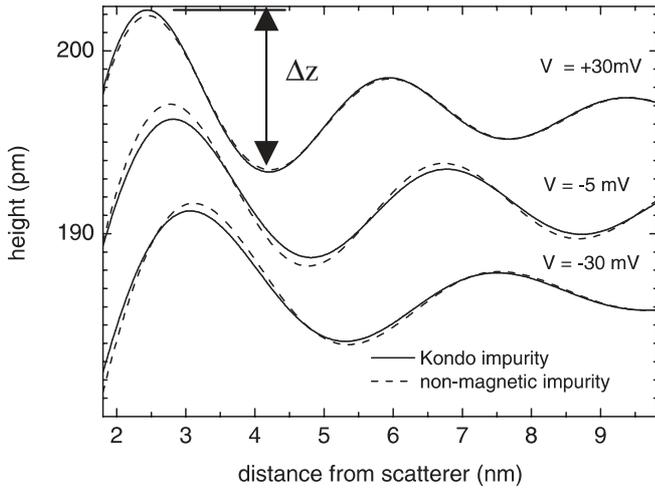
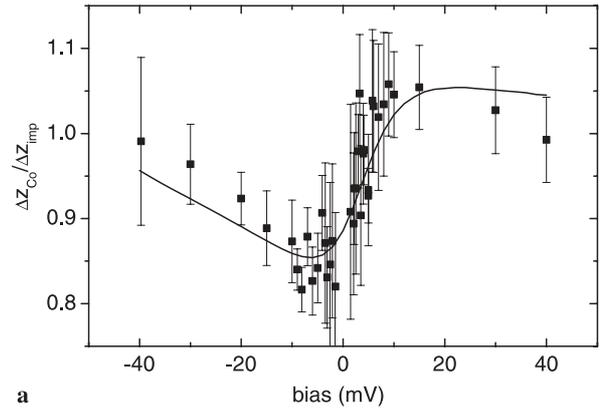
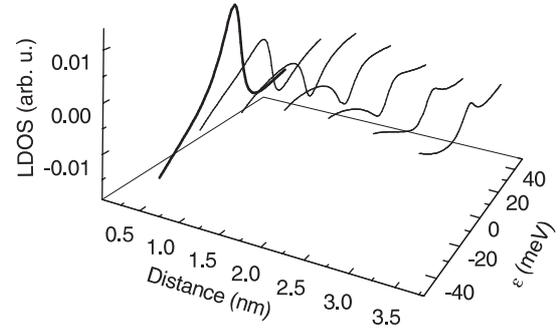


FIGURE 2 Calculated topography $z(r)$ around a Kondo impurity and a non-magnetic impurity for three different bias voltages V near the Fermi energy. An energy dependent phase shift $\delta(E)$ (4) is used to calculate the constant current topography around the Kondo impurity whereas an energy independent phase shift is used for the non-magnetic impurity. Due to absorptive scattering at the impurities the position of the maxima is a relatively insensitive measure of the elastic phase shift, the amplitude Δz , however, varies in magnitude as function of bias voltage to an extent measurable by STM

as determined from the on-atom spectrum (Fig. 1b) and the values for δ_{bg} and δ_{ab} which will follow from the full analysis (see below). The non-magnetic impurity is characterized by an energy independent complex phase shift δ_{imp} . As shown in Fig. 2 due to the strongly absorptive scattering of the impurities the elastic part of the phase shift $\delta(E)$ of the Co adatom which varies by π when sweeping the energy across the Fermi level produces hardly any difference in the positions of the oscillation extrema compared to those of the non-magnetic impurity. However, in direct comparison to the non-magnetic impurity the wave amplitude around a Kondo impurity varies with bias voltage to a degree which can be detected by STM. Therefore we define the oscillation amplitude $\Delta z(V)$ as being the height difference between the first maximum and second minimum of the oscillation pattern of the constant-current topography as function of bias voltage. We note Δz is measured 3 to 6 nm away from the scatterer in a region where no Kondo signature can be detected in dI/dV spectra and that Δz is purely related to the electrons in the surface state. The measurement of the ratio $\Delta z_{Co}/\Delta z_{imp}$ between the amplitudes around Co adatoms and non-magnetic impurities as function of bias V is shown in Fig. 3a. We find a characteristic voltage dependence which is caused by the resonance behavior of $\delta(E)$ of the Kondo impurity and reflects the interaction of surface-state electrons with the Co adatom. $\Delta z_{Co}/\Delta z_{imp}$ can now be used to fully determine the phase shift around a Co adatom at each energy point. To this end we fit the experimental data to the same quantity calculated from the inversion of (3) using the LDOS of (2) with a phase shift $\delta(E)$ according to (4) for the Co adatom and a complex energy independent phase shift δ_{imp} for the non-magnetic impurity. Following [26] we set the real part $\Re(\delta_{imp}) = \frac{\pi}{2}$. Since the dispersion $k(E)$, T_K , and ε_K are known, we are left with three fit parameters: δ_{bg} which determines the line shape of $\Delta z_{Co}/\Delta z_{imp}$, δ_{ab} which determines the depth of its minimum, and $\Im(\delta_{imp})$



a



b

FIGURE 3 (a) Measured dependence of the normalized wave amplitude $\Delta z_{Co}/\Delta z_{imp}$ as function of energy. The line is a fit given by the ratio of the calculated constant current topographies as in Fig. 2 using $\delta_{bg} = -0.24\pi$ and $\delta_{ab} = 0.97$ in (4) for the Co adatom. (b) calculated dI/dV spectrum at fixed positions according to the phase shift of (4). The line shape when reaching the apparent periphery of the adatom (~ 0.5 nm) is not converging towards the lineshape measured in Fig. 1b. (slowly varying background subtracted)

which determines its value for bias voltages far from the Fermi energy. We obtain $\delta_{bg} = -0.24\pi$ and $\delta_{ab} = 0.97$ for the Co impurity and $\delta_{imp} = \frac{\pi}{2} + 2.1i$ for the non-magnetic impurity (Fig. 3a).

A scattering problem is completely determined by the knowledge of the energy dependent scattering phase shift. Therefore we can analyze the corresponding line shape $dI/dV(r, E) \sim \Delta \varrho(r, E)$ as function of distance r due to the surface-state electrons interacting with the Kondo impurity. The result is shown in Fig. 3b. We see that the line shape oscillates with distance as expected from the work of Ujsaghy et al. [4]. However, the line shape for $r \rightarrow 0$ does not converge towards the measured dip (Fig. 1b). At 1 nm distance the line shape is clearly asymmetric and becomes peak-like at even shorter distances. We arrive at the important conclusion that for Co on Ag(111) the line shape that is measured at the position of the adatom is not determined by the interaction of the Co adatom with the surface-state electrons. This makes it unlikely that T_K is determined by the surface state. For the experiment of the “quantum mirage”, i.e., Co on Cu(111), Fiete et al. obtain a phase shift given by the background phase $\delta_{bg} = -0.25\pi$ [18]. An analysis like the one shown in Fig. 3b for Co on Cu(111) yields also a line shape that does not fully correspond to the one measured at the adatom position. However the difference is not that striking, here a more careful examination is needed.

In the Kondo model, T_K is given by an exponential dependence on the density of states at the Fermi level ρ_F and the antiferromagnetic coupling J ($J > 0$) between the impurity spin and the spins of the host electrons:[1]

$$T_K \propto e^{-\frac{1}{2J\rho_F}}. \quad (5)$$

Since this is a very sensitive dependence on the electron density at a certain site, one would expect a variation of T_K if the Co adatom is placed in the density modulations caused e.g., by a step edge. Completely analogous to the findings of Limot and Berndt who investigated this for Co on Ag(111) [24] we also do not find a dependence of T_K on the position of the Co adatom on Cu(111), Ag(111) or Au(111). Furthermore, an attempt to correlate the finding $T_K^{\text{Cu(111)}} < T_K^{\text{Au(111)}} < T_K^{\text{Ag(111)}}$ for Co adatoms with properties of the surface states of the three surfaces is not successful: the density of states in a 2DEG is proportional to the effective mass, which means that Cu(111) and Ag(111) should have rather similar T_K . Similar discrepancies can be found when looking at the surface-state binding energies or the projected bulk band edges at $\bar{\Gamma}$ of the surface Brillouin zone. The conclusion from these observations is that apparently the coupling J between the impurity spin of the Co 3d orbital and the surface-state electrons is rather small. The small coupling constant is consistent with findings of ab initio calculations of Co on Cu(111) in the framework of Green functions-KKR theory [27].

4 Tuning the Kondo temperature: interaction with bulk-state electrons

In the preceding section we have elucidated the role of a surface state in forming the Kondo many-body state. We now want to show that the Kondo temperature of magnetic surface impurities can be tuned by varying the strength of the chemical bond to the host metal crystal, i.e., the number of nearest neighbors to the impurity. This is achieved by either adsorbing the magnetic atom on different crystal faces, or by manipulating the adatom to a specific binding site (e.g., a step edge) with the tip of the STM. In effect this is similar to what can be realized by tuning the coupling of a quantum dot in the Kondo regime to the connecting leads [28]. We focus here on the Kondo system Co/Cu. Since the data is taken at adsorption sites with different (if any) weight of a surface state at E_F the scaling of the Kondo temperatures with the number of nearest neighbors shows the dominant character of the coupling of the impurity to the bulk states of the crystal also for Co/Cu. By manipulating a Co atom on Cu(111) to the rising step edge of the terrace it is adsorbed on we change its number of nearest neighbors from three to five. Furthermore near a step edge the surface state at E_F present on the Cu(111) is quenched. The dI/dV spectrum on the Co atom is shown in Fig. 4a. It has been obtained by subtracting the spectrum taken on the lower terrace some nm away from the step edge from that taken on top of the adsorbed atom. Apparently the step edge itself reduces the LDOS characteristically near the Fermi level for a large range of negative bias values. However, superimposed on that reduction of the signal is a small dip that we fit with the function given by (1). Due to the step influence there is a somewhat larger uncertainty in the obtained T_K value:

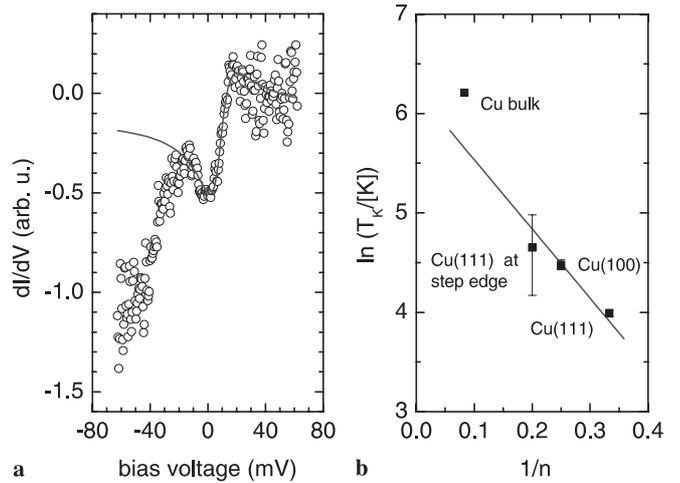


FIGURE 4 (a) Kondo resonance for a Co adatom bound to a step edge at Cu(111). The line is a fit to (1) and results in $T_K \sim 105$ K. Kondo temperatures of Co adatoms on Cu surfaces vs. number of nearest neighbors n at the specific surface or adsorption site. $n = 3$: Co on Cu(111); $n = 4$: on Cu(100); $n = 5$: at a step edge on Cu(111); $n = 12$: as substitutional bulk impurity (from [30])

$T_K = 105 \pm 40$ K. Using additional data from [11] for Co on the (111) and (100) surfaces, we can establish a trend that on copper surfaces the Kondo temperature rises with increasing coordination of the adsorbate. This is shown in Fig. 4b. We find that to a first approximation $\ln T_K$ varies linearly with $1/n$ where n is the number of nearest neighbors of the adsorbate. A recently published result of T_K of Co in the first layer of the Cu(111) surface also fits into that scaling behavior [29]. Since for the different results on the Cu(111) surface ρ_F is essentially constant, we come to the conclusion that $J \propto n$ in (5).

This result provides a microscopic view on the parameter J . The Kondo Hamiltonian leading to (5) uses J as an effective parameter describing the strength of the on-site spin interaction of impurity and conduction band electrons. Microscopically this interaction is mediated by the chemical bond of the impurity to the substrate. Employing a tight-binding picture, one could argue that the more bonds there are the stronger the interaction becomes. In consequence J becomes proportional to the number of bonds. However, in this simplistic view the coupling strength per bond is a constant characteristic of the Co–Cu system and does not reflect e.g., the fact that binding lengths vary between the various surface systems. Also, as one can see from the results of the Anderson model in which J becomes a function of energetic position and width of the magnetic impurity level, an increase in hybridization can produce much more subtle effects than just a monotonous increase in J [1]. Therefore a thorough investigation how the local (chemical) environment of the impurity determines its magnetic properties is still needed. It should lead to an explanation of the relative Kondo temperatures not only of the Co/Cu system but also of the Co surface impurity on different noble metal surfaces. Based on our results such an explanation need not consider the role of surface states but should incorporate the basic scaling idea demonstrated here for Co on Cu where a change of the number of neighboring substrate atoms induces a systematic change in the Kondo temperature of the adsorbate system.

5 Conclusions

We have presented STM and STS measurements of the properties of the Kondo many-electron state formed by Co adatoms on noble metal surfaces. Notwithstanding the large weight of the surface-state electrons at the surface and in the vacuum above the surface, we show that for the case Co on Ag(111) the surface state does not determine the measured resonant line shape. To this end we measured the scattering phase shift the surface-state electrons acquire when scattering off the fully spin-screened Co impurity. We argue that the reason for the low contribution towards the line shape lies in the small effective coupling of the Co d -levels to the surface-state electrons. This low coupling also explains why the Kondo temperature is neither influenced by details of the surface-state properties nor by the density modulations present near e.g., steps on the (111) surfaces. For Co impurities on copper surfaces we have shown that T_K increases with increasing number of nearest neighbors. Experimentally the measurements were taken on the Cu(111) and Cu(100) surface (three, respectively, four nearest neighbors) and at a step edge on Cu(111) (5 neighbors). We explain the increase in T_K by an increase of hybridization of the magnetic impurity with the bulk electronic system of the crystal. This establishes the general trend and should serve as a basis for a theoretical treatment of the hybridization of Co on surfaces involving all electronic states present. Such a treatment is still needed to e.g. explain the relation between the Kondo temperature of Co adsorbed on Cu compared to that of Co on Ag or Au.

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