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Kondo Effect of Co Adatoms on Ag Monolayers on Noble Metal Surfaces

M. Alexander SCHNEIDER, Peter WAHL, Lars DIEKHÖNER*, Lucia VITALI, Gero WITTICH and Klaus KERN

Max-Planck-Institut für Festkörperforschung, Heisenbergstr. 1, D-70569 Stuttgart, Germany

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The Kondo temperature T_K of single Co adatoms on monolayers of Ag on Cu and Au(111) is determined using Scanning Tunneling Spectroscopy. T_K of Co on a single monolayer of Ag on either substrate is essentially the same as that of Co on a homogenous Ag(111) crystal. Besides giving strong evidence that the interaction of surface Kondo impurities with the substrate is very local in nature the data show that the energy scale of the many-electron Kondo state is insensitive to the properties of surface states and to the energetic position of the projected bulk band edges. We demonstrate that the trend of the Kondo temperature of Co adatoms is correlated to the impurity's d-band shift as obtained from the Hammer and Nørskovs model of reactivity neglecting many-body effects. [DOI: 10.1143/JJAP.44.5328]

KEYWORDS: Kondo effect, electron correlation, many-body effects, scanning tunneling spectroscopy, single atom spectroscopy

1. Introduction

The interaction of a magnetic impurity with the electrons of a non-magnetic host serves as a paradigm of many-body physics. The explanation of the resistivity minimum of dilute magnetic alloys at low temperatures and the development of appropriate theoretical tools to understand the rich phenomenology of the Kondo effect[1,2] are still shaping the research now done in heavy fermion systems and Hi-Tc superconductivity.[3] Even in the domain of the classical Kondo effect interest has been renewed when two different experimental approaches became possible: one was to study the Kondo effect in quantum dots which behave like artificial "spin impurities",[4–6] the other was the use of the scanning tunneling micrsoscope (STM) to study the electronic properties of single magnetic atoms on metal surfaces.[7,8] We present here results of the latter technique.

The Kondo effect is due to the formation of a correlated singlet ground state at low temperatures in which the magnetic spin of the impurity is screened by a cloud of conduction band electrons interacting with the impurity. The formation of this state lowers the energy of the electronic system by the amount $k_B T_K$, where T_K is the Kondo temperature of the system which ranges from sub-Kelvin to several hundred Kelvin. As function of temperature T transport coefficients like resistivity, specific heat, and susceptibility depend on T/T_K, making T_K the fundamental parameter of the low energy excitations of the many-electron problem. The special properties of the transport coefficients are caused by the formation of a resonance at the Fermi energy in the single particle density of states of the impurity. Its half width is $k_B T_K$ for $T \ll T_K$.[3] Whereas transport measurements probe this resonance indirectly it has been directly probed by (normal and inverse) photoemission spectroscopy in the case of Kondo alloys that contain rare earth metals[9] and by scanning tunneling spectroscopy (STS) for 3d impurities at surfaces.[7,10–13] It has been a first concern to understand the mechanism by which the Kondo resonance peak in the impurity density of states is transformed into the Fano line shape seen by STS.[13–15] In contrast, here we are concerned with understanding what determines the Kondo temperature of a magnetic surface impurity. Recently, we have put forward a simple model based on a tight-binding approach to adatom hybridization that allows to understand the trends in T_K for Co on a variety of noble metal surfaces.[16] The experiments presented here support the tight-binding view since it appears that in an overlayer system T_K is determined by the chemical identity of the first surface layer.

2. Experimental

Single crystal surfaces were prepared by standard sputtering and annealing cycles in ultra-high vacuum (base pressure $1 \cdot 10^{-10}$ mbar). For the experiments on overlayer systems Ag was evaporated from an electron beam heated source at room temperature. 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 deposition 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 $\mathrm{mV_{RMS}}$ at a frequency of 4.5 kHz. All bias voltages are sample potentials measured with respect to the tip.

3. Results

In Fig. 1 we compare the experimental dI/dV spectra taken with the STM-tip on top of a Co adatom on 1 monolayer (ML) of Ag on Cu(111) with those of a Co adatom on the clean (111) surfaces of Cu and Ag. By preparing islands of Ag on Cu(111) we were able to probe Co on Cu(111) and Co on Ag/Cu(111) with the same microscopic STM tip. Therefore a broadening of the Ag/Cu(111) spectra due to experimental artifacts can be excluded. [The Co on Ag(111) spectrum was taken with a different tip on a Ag(111) crystal.] The spectra were fitted to the line shape given by the Fano expression:

$$\frac{\mathrm{d}I}{\mathrm{d}V} \propto \frac{(q+\epsilon)^2}{1+\epsilon^2} \qquad (1)$$

where $\epsilon = \frac{eV-\epsilon_K}{\Gamma}$ is the normalized energy and ϵ_k is the position of the resonance of width Γ relative to the Fermi energy.[14,15] In the following we will identify the Kondo

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*Corresponding author. Present address: Aalborg Universitet, Institut for Fysik og Nanoteknologi, Pontoppidanstraede 103, DK-9220 Aalborg, Denmark.
E-mail address: ld@physics.aau.dk

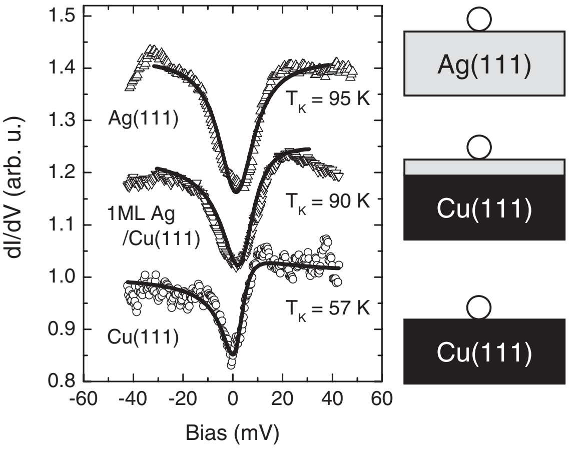

Fig. 1. Comparison of experimental dI/dV spectra taken with the tip above a single Co adatom on a 1ML Ag film on Cu(111) with that on the clean Cu(111) and Ag(111) surfaces. Spectra are fitted to eq. (1) with T_K as indicated, average values of sets of measurements are given in Table I. For 1ML of Ag the width of the resonance which is proportional to T_K is already that of the adatom on Ag(111).

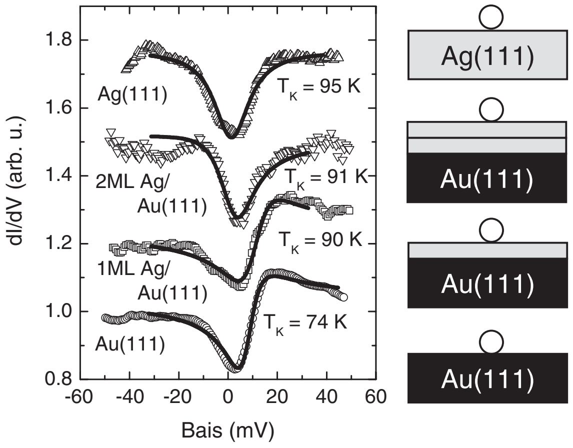

Fig. 2. Same as Fig. 1 but for a Co adatom on 1 and 2 ML of Ag on Au(111) compared to Au(111) and Ag(111). Already for 1ML of Ag the resonance width is the same as that of the adatom on Au(111).

temperature T_K with the half width Γ/k_B of the measured resonance. We find that for a Co adatom on one ML of Ag on Cu(111) T_K is within the error bounds the same as that of a Co adatom on Ag(111). A systematic study of the influence of the known reconstruction of the Ag film on Cu(111) was not yet undertaken. We expect, however, that it will be similar to the situation encountered at Au(111). Here an influence of the surface reconstruction on the line shape but not on T_K was observed.[18]

The spectra of single Co adatoms on 1 or 2 ML of Ag on Au(111) are shown in Fig. 2. They yield the same finding as the Ag/Cu(111) case. In the Ag/Au case it becomes more obvious that the line shape (parameter q) is a function of Ag layer thickness. The line shape is related to the electronic structure of the host and the balance between tunneling into adsorbate and into host electronic states respectively.[7,8,14,15] Since q of Co on the Ag overlayer systems deviates from that of Co on Ag(111) whereas T_K does not, this parameter apparently reflects single-particle electron wave functions and scattering processes rather than the many-electron properties of the systems which we focus on in this paper. What can already be seen is that electronic properties on length scales much shorter than the spin-correlation length (expected to be of the order 100 nm in the systems studied here) determine T_K.

In Table I we summarize the average T_K of the resonance of Co adatoms on the various surfaces that are of concern here. We also quote the Fano-parameter q, parameters of the surface state at $\bar{\Gamma}$ like the onset energy E_0, and effective mass m^*, as well as the band edge positions of the sp-bands at the L-point of the bulk Brillouin zone $E_{L_{2'}}$ and E_{L_1}, and the work function ϕ. The purpose of the latter parameters is to discuss in the following whether they play a decisive role in determining the measured Kondo temperatures of Co adatoms.

T_K of a magnetic impurity system depends very sensitively on the details of the hybridization of the atomic levels of the impurity with the host electronic system. In fact, from the Kondo model it follows that

$$T_K \approx D e^{-\frac{1}{2J\rho_F}} \tag{2}$$

where D is the width of the substrate band, J is the antiferromagnetic ($J > 0$) coupling of the impurity spin with the spins of the substrate electrons and ρ_F is the substrate's density of states at the Fermi energy. J depends on the coupling matrix elements of the host electrons with the impurity. The exponential dependence of T_K on J makes T_K very sensitve to details of adatom hybridization allowing to discuss the contribution of different bands towards J.

4. Discussion

First we want to discuss whether the properties of the (111)-surface state determine T_K. If we look at the surface-state band in these systems, we see that a change in E_0 or m^*

Table I. Average Kondo temperature T_K and line shape parameter q for Co adatoms on noble metal surfaces and monolayer systems. Also given are the surface state onset E_0 and its effective mass m^*, the bulk band edge energies at L $E_{L_{2'}}$ and E_{L_1}, and the work-function ϕ. For the overlayer systems $E_{L_{2'}}$ and E_{L_1} were taken to be those of the underlying bulk crystal, whereas ϕ was assumed to be that of Ag. All energies are given relative to the Fermi energy. (* denotes data measured in this paper)

Substrate	T_K/K	q	E_0/eV	m^*/m_0	$E_{L_{2'}}$/eV	E_{L_1}/eV	ϕ/eV
Cu(111)	54 ± 2[10,12]	0.2	−0.44[19]	0.38[19]	−0.9[23]	4.25[23]	4.94[23]
Au(111)	76 ± 8[*,7]	0.7	−0.51[20]	0.27[20]	−1.0[23]	3.6[23]	5.55[23]
Ag(111)	92 ± 6[13]	0.0	−0.065[19]	0.40[19]	−0.4[23]	3.9[23]	4.56[23]
1ML Ag/Au(111)	88 ± 10*	0.8	−0.27[24]	0.3[24]	−1.0	3.6	4.56
2ML Ag/Au(111)	95 ± 10*	−0.1	−0.2[24]	0.4[24]	−1.0	3.6	4.56
1ML Ag/Cu(111)	92 ± 10*	0.15	−0.23[22]		−0.9	4.25	4.56

does not cause a systematic change in T_K. Although in the overlayer systems the surface-state onset energy will shift only within the first 5–10 Ag layers to the value of the Ag(111) surface,[21,22] there occurs no change in T_K after the first layer. Furthermore, since $\rho_F = \frac{m^*}{\pi\hbar^2}$ for a two-dimensional electron gas, the surface-state properties would not only enter eq. (2) via the band width but also via ρ_F. We note that systematic changes in T_K due to the surface-state band are not observed.

It was argued by Lin *et al.*[25] that the surface-state electrons play a major role in the formation of the Kondo state for Co on Cu(111) through their dominant contribution to J. Most of that dominance is linked to the fact that surface-states are naturally normalized to an area rather than a volume leaving the decay of the state into the bulk crystal as a weight determining parameter. To see whether the mere presence of a surface state together with its decay determines T_K we argue that in Ag(111) the surface state is almost like a surface resonance with weight up to the 10th crystal layer from the surface[26] whereas in Cu(111) the surface state decays much more rapidly. Consequently, the weight of the surface state at the surface is much smaller in Ag(111) than in Cu(111). By producing an overlayer of 1ML Ag on Cu(111) the surface state still decays rapidly into the bulk and one would therefore expect a similar contribution of this state to T_K as on the unmodified Cu(111) which appears not to be the case.

The decay of the surface state into the bulk is related to the positions of the bulk band edges at L. The band edges determine the energetic positions of states with large momentum perpendicular to the surface plane that could lead to differences in the hybridization of the Co adatom. However, inspection of Table I tells that this does not influence T_K: in the overlayer systems the bulk electron states are unchanged and so is the bandgap at L, but T_K deviates greatly from that of the impurity on the clean host crystal.

Finally, also the surface dipole, i.e. the work function, can be shown not to influence T_K. If the decay length of wave functions into the vacuum and the adsorbate position relative to the surface layer determined T_K this would explain why T_K on the overlayer systems is that of Co on Ag(111). However, Co on Cu(111) would have the highest degree of hybridization due to its short binding length (as estimated from a hard sphere model) followed by Ag(111) and then by Au(111) due to $\phi^{\mathrm{Ag}} < \phi^{\mathrm{Au}}$. This is in contradiction to $T_K^{\mathrm{Au}} < T_K^{\mathrm{Ag}}$. From the data presented here we can therefore conclude that changes in the sp-bandstructure including the surface states on the noble metal (111) surfaces do not induce a change in the Kondo temperature of magnetic adatom systems. This leads us to the conclusion that the interaction determining the Kondo temperature of a surface impurity system is very local in nature, probably involving the d-orbitals of the substrate atoms.

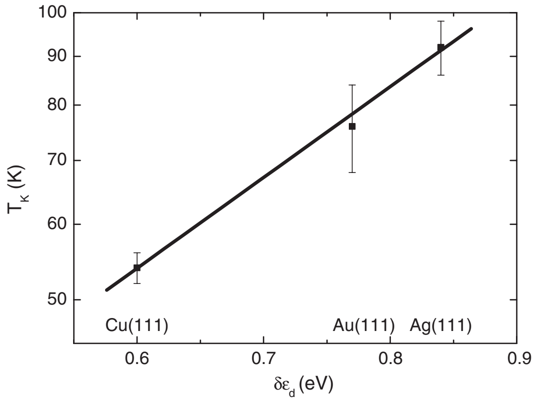

Fig. 3. Logarithmic plot of the Kondo temperature of single Co adatoms on Cu, Au, and Au(111) plotted vs the d-level shift $\delta\epsilon_d$ calculated with LMTO-ASA[28] for Co in the first crystal layer.

A key to understanding the trend of Kondo temperatures of single magnetic surface impurities could lie in studying connections between calculated single particle properties and their mapping onto the many-body problem. We would like to discuss such an example in the following to trigger more theoretical investigations. To do so, we have to use the expression for the Kondo temperature in the more general single impurity Anderson model instead of the Kondo model [eq. (2)]. In the Anderson model the coupling constant J is replaced by (Schrieffer-Wolff transformation[27]):

$$\frac{1}{J} = \frac{\pi\rho_F}{\Delta U}\,|\epsilon_d| \cdot |\epsilon_d + U| \tag{3}$$

where ϵ_d is the energy of the impurity level, Δ its width acquired through hybridization, and U is the on site Coulomb repulsion. When comparing T_K values of a specific impurity (in our case Co) on different host metals a strong variation in T_K is expected from changes in ϵ_d as this can vary by hundreds of meV. In Fig. 3 we demonstrate that there exists a linear relation between the calculated $\delta\epsilon_d$ for Co as a first layer impurity[28] and the logarithm of the measured T_K for the three systems Cu, Au and Ag(111). The calculated $\delta\epsilon_d$ were originally used in conjunction with the model by Hammer and Nørskov to understand trends in the reactivity of transition and noble metal surfaces.[29]

The observed relation between $\delta\epsilon_d$ and T_K indicates that the trend of the Anderson model ϵ_d for the three surfaces can be written as $\epsilon_d = \epsilon_{d0} + \delta\epsilon_d$ where ϵ_{d0}, and Δ and U do not vary between the three systems or are a property of the adatom. We note that the calculation of ref. 28 predicts the lowest degree of hybridization for Co on Ag(111) and the highest for Cu(111) consistent with our earlier observation of a simple scaling law for T_K of Co on other noble metal surfaces.[16]

A similar relation can be found between T_K and the calculated orbital moments of Co in Ag, Au, and Cu.[30] An interesting aspect of this is that it might lead to an understanding of the interplay between Kondo physics, spin-orbit coupling and the magnetic anisotropy energy.[31] At surfaces the anisotropy energy of single impurities can reach values comparable to the Kondo temperatures discussed here.[32]

5. Summary

In conclusion, we have determined the Kondo temperature T_K of single Co adatoms in interaction with Ag mono- and bilayers on Cu(111) and Au(111) by STS and compare the results to T_K found for Co on the (111) surfaces of Cu, Ag and Au. We observe that T_K on the Ag overlayers is that of the Co adatom on Ag(111) already for the first monolayer of

Ag on either Cu or Au(111) despite the fact that $T_K^{\mathrm{Cu}} < T_K^{\mathrm{Au}} < T_K^{\mathrm{Ag}}$ for the homogenous substrates. We find that properties of the surface states and the energetic positions of the sp-derived bulk bands found in these substrates cannot explain the trend in T_K. Since the topmost crystal layer determines T_K it is suggested that a more local interaction of the Co d-levels with the d-bands of the host metal is decisive. To further explore the Kondo properties of Co on the noble metal (111) surface a correlation of the trend of T_K with the trend of the calculated shift of the impurity's d-level on the different surfaces is shown. These single-electron calculations have been used to explain the reactivity of 3-d impurity sites at surfaces. The link between chemistry at the surface and the many-body Kondo effect is established by the fact that both properties depend sensitively on the details of the impurity-host interaction. This observation might be useful to gain a deeper understanding of the Kondo physics of adatom systems.

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