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

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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]

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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. 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 effect⁴⁻⁶ are still shaping the research now done in heavy fermion systems and Hi-Tc superconductivity.⁴⁻⁵ 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 microscope (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 $k_BT_K$, 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 $k_BT_K$ for $T \ll T_K$.⁹ 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 metals⁹ 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 $1 \text{mV}_{\text{RMS}}$ 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:

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

where $\epsilon = \frac{eV + \epsilon_F}{k_BT}$ is the normalized energy and $\epsilon_F$ is the position of the resonance of width $\Gamma$ relative to the Fermi energy.¹⁴⁻¹⁵ In the following we will identify the Kondo

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temperature $T_K$ with the half width $\Gamma/k_B$ 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 overlay 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 $\Gamma$ 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 $E_{\text{L},s}$ and $E_{\text{L},p}$, and the work function $\phi$. 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

$$T_K \approx D e^{-\frac{J^2}{4D^2}}$$

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 $\phi_F$ 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 sensitive 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 $m^*$
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, there occurs no change in $T_K$ after the first layer. Furthermore, since $\rho_F = \frac{\rho_0}{N}$ for a two-dimensional electron gas, the surface-state properties would not only enter $\text{eq. (2)}$ via the band width but also via $\rho_F$. We note that systematic changes in $T_K$ due to the surface-state band are not observed.

It was argued by Lin et al. 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 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 $\phi_{Ag} < \phi_{Cu} < \phi_{Au}$. This is in contradiction to $T_K^{Ag} < T_K^{Cu}$. From the data presented here we can therefore conclude that changes in the sp-bandstructure including the d-orbitals of the substrate atoms. 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):

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

where $\epsilon_d$ is the energy of the impurity level, $\Delta$ 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 $\epsilon_d$, 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 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 Norskov to understand trends in the reactivity of transition and noble metal surfaces.

The observed relation between $\delta\epsilon_d$ and $T_K$ indicates that the trend of the Anderson model $\epsilon_d$ for the three surfaces can be written as $\epsilon_d = \epsilon_{d0} + \delta\epsilon_d$ where $\epsilon_{d0}$, and $\Delta$ 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.

A similar relation can be found between $T_K$ and the calculated orbital moments of Co in Ag, Au, and Cu. 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. At surfaces the anisotropy energy of single impurities can reach values comparable to the Kondo temperatures discussed here.

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 $T_K^{Cu} < T_K^{Au} < T_K^{Ag}$ 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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