

Kondo Temperature of Magnetic Impurities at Surfaces

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Based on the experimental observation that only the close vicinity of a magnetic impurity at metal surfaces determines its Kondo behavior, we introduce a simple model which explains the Kondo temperatures observed for cobalt adatoms at the (111) and (100) surfaces of Cu, Ag, and Au. Excellent agreement between the model and scanning tunneling spectroscopy experiments is demonstrated. The Kondo temperature is shown to depend on the occupation of the d level determined by the hybridization between the adatom and the substrate with a minimum around single occupancy.

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Understanding the physics of a single spin supported on a metal host is at the basis of a bottom up approach to the design of high density magnetic recording [1]. The effects occurring in the limit of very small magnetic structures can be studied macroscopically on dilute magnetic alloys or microscopically for single magnetic impurities [2,3] and spins in quantum dots [4,5]. These systems develop a rich phenomenology, which is commonly referred to as the Kondo problem [6]. It deals with the interaction of a magnetic impurity with the conduction electrons of a surrounding nonmagnetic metal host. This interaction leads to the screening of the spin of the impurity and in consequence to anomalies in the macroscopic properties. A many body ground state is formed at temperatures well below the Kondo temperature T_K . Once the Kondo temperature of a given system is known, its behavior at low temperatures is completely determined. The first experimental evidence became available 70 years ago by measurements of the resistivity of nonmagnetic metals with minute amounts of magnetic impurities [7] which showed an anomalous behavior below T_K . It is only recently that interest has been revived through the investigation of Kondo phenomena in quantum dots on one hand, providing model systems, which allow tuning of the relevant Kondo parameters easily [4,5], and of single magnetic impurities using low temperature scanning tunneling microscopy (STM) and spectroscopy (STS) on the other hand. The spectroscopic signature of the Kondo effect, the Kondo resonance, of single adatoms has been first observed by STS for cobalt adatoms on Au(111) [2] and cerium on Ag(111) [3].

The Kondo resonance shows up as a sharp peak in the local density of states, which is pinned to the Fermi level and has a width proportional to T_K . Since the first measurements on single magnetic impurities, several other Kondo systems at noble metal surfaces have been reported [8–10]. Although previously systematic studies of the Kondo effect of impurities on surfaces have been performed [10], it is still unclear what determines the Kondo behavior of a specific adatom-substrate system.

In this Letter, we present a comprehensive study of the Kondo resonance of single cobalt adatoms on different noble metal surfaces as well as on a heteroepitaxial system, namely, Ag on Cu(111). Based on the observation that the Kondo behavior is governed by the immediate vicinity of the impurity, we introduce a simple model that describes the coupling between adatom and substrate and allows us to predict the properties of the Kondo systems. The derived scaling behavior is in perfect agreement with available experimental data for cobalt adatoms on noble metal surfaces.

The measurements have been performed in a home-built low temperature ultrahigh vacuum (UHV) STM operating at 6 K. The single crystal Cu(111) and Ag(100) surfaces have been carefully prepared by argon ion sputtering and annealing cycles in UHV (base pressure 1×10^{-10} mbar). Adatoms have been evaporated from a cobalt wire wound around a tungsten filament onto the surface at ≈ 20 K. Typical coverages were around 0.001 ML. The Ag monolayer has been deposited from an e -beam evaporator. Spectroscopic measurements were performed with an open feedback loop using a lock-in technique with a modulation of the sample voltage of 1–1.5 mV_{rms} at a frequency of 4.5 kHz. All bias voltages are sample potentials measured with respect to the tip and energies are given with respect to E_F . Spectra shown in this Letter are background subtracted [11], which means that a spectrum taken on a clean spot of the surface is subtracted from the spectrum taken on the atom with the same tip. This removes artifacts due to slowly varying features in the tip spectrum. For the measurements presented here, an iridium tip, cut from a wire and mechanically ground, has been used.

The tunneling conductance with the tip placed on top of a magnetic adatom can be described by the well known Fano formula [12,13]

$$\frac{dI}{dV} \sim \frac{(q + \tilde{\epsilon})^2}{1 + \tilde{\epsilon}^2}, \quad (1)$$

where $\tilde{\epsilon} = \frac{\omega - \epsilon_k}{T}$, $\omega = eV$ (e is the elementary charge). It describes the line shape due to the hybridization of the

Kondo state with the conduction band electrons. The shape of the Fano function is determined by q and can vary between a dip for $q = 0$, an asymmetric line shape for $q \approx 1$, and a peak for $q \rightarrow \infty$. ϵ_K defines the position of the resonance relative to E_F and Γ , its half width. The latter is proportional to the Kondo temperature T_K [14]. Although there has been considerable effort in describing the adatom-substrate system theoretically, it is still unclear whether the line shape as observed in STS experiments and hence q are determined rather by interfering tunneling channels [15] or by the electronic structure of the substrate [16,17].

Typical tunneling spectra, which we measure with the tip placed above a single cobalt adatom, are shown in Fig. 1. For Ag(100), the spectrum shows a distinct dip slightly above the Fermi energy. The line shape is the same as for Co/Ag(111) [9] while the Kondo temperature is 41 ± 5 K. The Kondo temperature has been averaged for several different atoms and tips. The value of the Kondo temperature for Co/Ag(100) is lower than that for Co/Ag(111). This indicates that the scaling of the Kondo temperature solely based on the number of nearest neighbors of the cobalt impurity as proposed for cobalt on copper surfaces [8] has to be amended.

Experiments on heteroepitaxial monolayers do prove, however, that the Kondo behavior of surface impurities is essentially determined by the interaction with its nearest neighbors. To demonstrate this, we have deposited one monolayer of Ag on the Cu(111) substrate at room temperature and subsequently deposited single cobalt adatoms on top as described above. The spectra recorded are shown in Fig. 1. The Kondo temperature of the adatom on one monolayer of silver on Cu(111) is already the same as on a bulk silver sample, although the Kondo temperatures

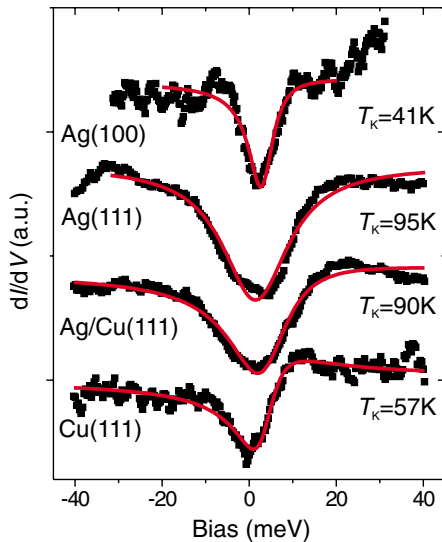


FIG. 1 (color online). Spectra taken on a cobalt adatom on Ag(100) as well as on cobalt adatoms on Ag(111), one monolayer of Ag on Cu(111), and on Cu(111). The solid lines depict the fit of a Fano line shape [Eq. (1)] to the data.

of Ag and Cu differ by almost a factor of 2. It is evident that the Kondo behavior is governed by the interaction with the nearest neighbors of the impurity. The Kondo temperatures as well as the line shapes for Cobalt adatoms on noble metal surfaces are listed in Table I.

Based on the observation that the Kondo resonance is governed by local interactions, we propose a model which explains the observed trend in the Kondo temperatures and the position of the resonance ϵ_K . In the Anderson model, which describes the behavior of a paramagnetic impurity in a nonmagnetic host metal, the Kondo temperature T_K can be calculated from [6]

$$k_B T_K \sim \sqrt{\frac{\Delta U}{2}} e^{-(\pi/2\Delta U)|\epsilon_d + U||\epsilon_d|}. \quad (2)$$

This equation relates the Kondo temperature T_K to the on site Coulomb repulsion U , the half width of the hybridized d -level Δ and its position ϵ_d . As can be easily seen, it is a monotonous function in U and Δ , while it has a minimum for $\epsilon_d = -\frac{U}{2}$ rising with either increasing or decreasing ϵ_d . Related to the position ϵ_d is the shift of the Kondo resonance ϵ_K with respect to the Fermi level. Because of level repulsion, the Kondo resonance is shifted to energies above ϵ_F for $\epsilon_d > -\frac{U}{2}$ and to lower energies for $\epsilon_d < -\frac{U}{2}$. Table I shows together with the Kondo temperatures the experimentally determined shift ϵ_K of the Kondo resonance with respect to the Fermi level. The values of ϵ_K indicate that the position of the d level varies considerably for the different adsorbate-substrate systems. It is positive for the (111) surfaces, rising with the Kondo temperature when changing the substrate from Cu to Ag to Au. For the (100) surfaces, the shift is increasing as well when going from Cu to Ag, but the Kondo temperature is decreasing, indicating that the Kondo temperature has a minimum as a function of the position of the resonance. Closely related to the position ϵ_d and the on site Coulomb repulsion, U is the occupation of the d -level n_d , which is larger than 1 for $\epsilon_d < -\frac{U}{2}$. Based on the experimental values of ϵ_K , one can readily establish a trend in ϵ_d and n_d .

Following Újsághy *et al.* [13], Eq. (2) can be expressed in terms of the occupation $n_d = -\frac{\epsilon_d}{U} + \frac{1}{2}$ of the d level. Thus the properties of the adatom as derived from a single particle model can be mapped on an effective spin- $\frac{1}{2}$ Anderson model. This results in

$$k_B T_K \sim \sqrt{\frac{\Delta U}{2}} e^{-(\pi U/2\Delta)|-n_d + 3/2||-n_d + 1/2|}. \quad (3)$$

As discussed above the behavior of T_K can be understood in terms of the position of the d level. Therefore we keep Δ and U constant and use $\Delta = 0.2$ eV and $U = 2.84$ eV as calculated for Co/Au(111) by Újsághy *et al.* [13]. n_d can vary between 0 (empty orbital) and 2 (double occupancy), where the Kondo regime is roughly $0.8 < n_d < 1.2$ [21] with approximately one unpaired electron in the d level.

TABLE I. Summary of Kondo temperatures for cobalt adatoms on the noble metal surfaces together with the parameters a and n_{NN} which enter our model. β is calculated according to Eq. (4) and n_d is obtained from the fit of Eqs. (3)–(5) as described in the text.

Substrate	T_K [K]	q	ϵ_K [meV]	a [Å]	n_{NN}	β	n_d	Reference
Cu(111)	54 ± 2	0.18 ± 0.03	1.8 ± 0.6	2.53	3	0.239	0.94	[8]
	53 ± 5	2.53	3	0.239	0.94	[18]
Cu(100)	88 ± 4	1.13 ± 0.06	-1.3 ± 0.4	2.53	4	0.319	1.16	[8]
Ag/Cu(111)	92 ± 10	0.15 ± 0.10	2.3 ± 1.0	2.7	3	0.202	0.84	This work.
Ag(111)	92 ± 6	0.0 ± 0.1	3.1 ± 0.5	2.7	3	0.202	0.84	[9]
Ag(100)	41 ± 5	0.0 ± 0.2	2.0 ± 1.1	2.7	4	0.269	1.02	This work.
Au(111)	76 ± 8	2.695	3	0.203	0.84	[19]
	75 ± 6	0.60 ± 0.05	6.5 ± 0.5	2.695	3	0.203	0.84	[20]

We assume that the change in occupation of the d level for cobalt adatoms and therefore n_d on the various noble metal surfaces discussed here can be estimated by a simple model which considers the hybridization between the d orbitals of the impurity with the neighboring substrate atoms. The occupation is assumed to increase with increasing overlap due to $sp-d$ hybridization [22,23]. The hybridization of the d orbital with the states of the substrate is described by a tight-binding-like hopping term [24]

$$\beta = n_{\text{NN}} e^{-a/\lambda_d}, \quad (4)$$

with a prefactor n_{NN} which takes the number of nearest neighbor substrate atoms into account. a denotes the distance between the center of the adatom and of the next substrate atom which we calculate within a hard sphere model. The values used in the calculation are tabulated in Table I. The spatial extent of the d orbital is assumed to be $\lambda_d \approx 1$ Å. The adatom resides in the hollow site on both types of surfaces discussed here, yielding $n_{\text{NN}} = 4$ for the (100) surfaces and $n_{\text{NN}} = 3$ for the (111) surfaces. To first order, n_d is described in terms of the hybridization by

$$n_d = n_{d0} + c\beta. \quad (5)$$

We use three fitting parameters in our model to explain the experimentally determined values of T_K and ϵ_K as summarized in Table I: n_{d0} , c , and the proportionality constant in Eq. (3). The resulting curve $T_K(n_d)$ is shown in Fig. 2(a), where the Kondo temperature is plotted as a function of n_d as determined from Eqs. (4) and (5). It shows an excellent agreement with the experiments. The parameters extracted from the fit are $n_{d0} = 0.28$, $c = 2.78$, and for the proportionality constant 2.08. As expected, the hybridization between the impurity and the conduction electrons and thus the occupation of the d level varies in a narrow range around $n_d \approx 1$. The trend in the occupation of the d level is confirmed by the position ϵ_K of the Kondo resonance. The relation between n_d and ϵ_K is plotted in Fig. 2(b) together with the theoretically expected behavior [6]:

$$\epsilon_K = \Gamma \tan\left[\frac{\pi}{2}(1 - n_d)\right]. \quad (6)$$

The systems cobalt on Cu(111) and Ag(100) are almost perfectly described by the symmetric Anderson model, where $n_d = 1$ and the Kondo temperature as a function of the occupation has a minimum. Either by enhancing the hybridization, i.e., by changing the substrate to Cu(100), or by reducing it by going to Ag(111) or Au(111) the Kondo temperature is rising. The value, which we find for the occupation of the d level for Co/Au(111), 0.84 is close to the calculated value 0.8 [13]. The physical picture that emerges is that for noninteger occupation the spin flip probability is higher and thus the Kondo temperature increases.

The key result is that based on simple arguments one finds an increasing occupation of the impurity level expressed in the value of n_d when going from a Ag(111) substrate to Cu(100) which explains the observed values of T_K and ϵ_K using the mapping onto the Anderson model

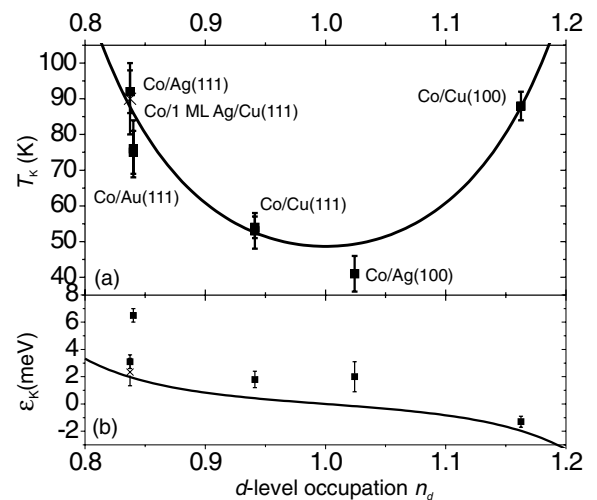


FIG. 2. (a) Kondo temperature T_K as a function of the occupation n_d of the d level calculated with Eqs. (3)–(5). (b) Shift of the Kondo resonance ϵ_K with respect to the Fermi energy; the solid line shows the prediction by our model according to Eq. (6).

proposed in Ref. [13]. The limitations of the simple model are obvious. It neglects relaxation, which can lead to an enhanced hybridization between the d level and the substrate. Furthermore, details of the electronic structure of the substrates are ignored. For Co/Au(111) the Kondo temperature is slightly lower than predicted by our model. This fact reflects that the model does not take into account hybridization with specific substrate orbitals. While the $4d$ orbitals of silver are very localized and well below the Fermi energy, the $5d$ orbitals of Au are close to the Fermi level and will contribute to the hybridization with the impurity. Thus the overlap is most likely underestimated for gold and overestimated for silver. Finally, the model neglects that an enhanced hybridization will lead to a reduction of the Coulomb repulsion U and an increase in the width of the d -level Δ . T_K increases monotonically as a function of both smaller U and larger Δ . Taking the variation of both into account will render the curve shown in Fig. 2(a) asymmetric and its minimum will be shifted to lower occupations but qualitatively show the same trend. This explains the systematic deviation of the shift ϵ_K in Fig. 2(b) from the calculated curve. We note that the surface state does not play a major role. Although its onset on Ag(111) is 165 meV closer to E_F than on Ag/Cu(111) [25], the Kondo temperature of a cobalt adatom is the same. This is consistent with our model, where the properties of the surface state do not enter and with earlier experimental [8,9] and theoretical results [26], both of which show that the surface state has only a minor influence on the properties of Kondo systems.

The behavior of the Kondo temperature as shown in Fig. 2(a) is similar to what has been measured on quantum dots. There, the properties of the Kondo system are tuned by varying a gate voltage, which shifts the electronic states up or down and thus decreases or increases the fractional occupation of the quantum dot [5]. In the case of adatom-surface systems, this tuning can be achieved by modifying the substrate.

In conclusion, we have presented a simple model in order to understand the large range of Kondo temperatures of cobalt adatoms on noble metals surfaces which have been reported previously and in this work. The model estimates the hybridization between the adatom's d level and the substrate. Despite the simplicity of this model, which is in contrast to the complexity of the many body physics necessary to describe the Kondo effect, it captures the essence of the impurity-substrate Kondo systems presented here. Motivated by experiments on Ag/Cu(111), only the local environment of the impurity enters our model. The Kondo temperatures for adatoms on multilayer systems is shown to depend only on the top-most layer. This conclusion is not trivial, since the extent of the Kondo cloud—the size of the many body state which leads to the formation of the Kondo resonance—is believed to be on the order of several ten to hundred

nanometers [27]. Because of the local character of the magnetic interaction, it will be interesting to investigate the behavior of a Kondo impurity on a surface alloy as a substrate, which should allow for a fine tuning of the Kondo temperature as a function of the local stoichiometry in the vicinity of the adatom.

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