Quantifying the leading role of the surface state in the Kondo effect of Co/Ag(111)

M. Moro-Lagares, J. Fernández, P. Roura-Bas, M. R. Ibarra, A. A. Aligia, and D. Serrate

1 Instituto de Nanociencia de Aragón, Laboratorio de Microscopías Avanzadas, University of Zaragoza, E-50018 Zaragoza, Spain
2 Institute of Physics, Academy of Sciences, 18221 Prague, Czech Republic
3 Regional Centre of Advanced Technologies and Materials, Faculty of Science, Department of Physical Chemistry, Palacky University, 78371 Olomouc, Czech Republic
4 Centro Atómico Bariloche and Instituto Balseiro, Comisión Nacional de Energía Atómica, 8400 Bariloche, Argentina
5 Departamento Física Materia Condensada, University of Zaragoza, E-50018 Zaragoza, Spain

Using a combination of scanning tunneling spectroscopy and atomic lateral manipulation, we obtained a systematic variation of the Kondo temperature \( T_K \) of Co atoms on Ag(111) as a function of the surface-state contribution to the total density of states at the atom adsorption site \( \rho_s \). By sampling the \( T_K \) of a Co atom on positions where \( \rho_s \) was spatially resolved beforehand, we obtain a nearly linear relationship between the magnitudes. We interpret the data on the basis of an Anderson model including orbital and spin degrees of freedom [SU(4)] in good agreement with the experimental findings. The fact that the onset of the surface band is near the Fermi level is crucial to finding the observed linear behavior. In light of this model, the quantitative analysis of the experimental data evidences that at least a quarter of the coupling of Co impurities with extended states takes place through the hybridization to surface states. This result is of fundamental relevance in the understanding of Kondo screening of magnetic impurities on noble-metal surfaces, where bulk and surface electronic states coexist.

DOI: 10.1103/PhysRevB.97.235442

I. INTRODUCTION

Single atoms with partially filled \( d \) or \( f \) shells on a solid-state surface are known to exhibit strong electron correlations leading to a wide range of physical ground states. The magnetic properties of such impurities on metals are inherently connected with many-body interactions between the localized magnetic moment and the conduction electrons [1–9]. In this framework, the Kondo effect [1,10,11] is the one most frequently found. Since this phenomenon is an archetypal example of the formation of a many-body quantum state, it is central to the understanding of the electronic behavior of complex strongly correlated electrons systems such as heavy fermions [11,12], Kondo insulators [13], and nanoscale systems [2,3,5,14–27].

Thanks to the large spatial and energy resolution of scanning tunneling microscopy (STM) and spectroscopy (STS) [2,18,19], these tools are extremely well suited to accessing the spectroscopic features of adsorbate-induced many-body resonances in tunneling differential conductance \( (dI/dV) \). Most STM studies on Kondo impurities are performed on noble-metal (111) surfaces, where bulk and surface electrons coexist [2,3,5,19–28]. Unavoidably, the question of whether surface or bulk electrons play the leading role in the Kondo effect arises. To date, the answer remains unclear because there are conflicting conclusions depending on the technical approach to the problem. Since bulk electrons decay much faster than surface-state electrons into the crystal, it has been common practice to measure the Kondo resonance as a function of the lateral distance to the atom [3,5,29,30].

For instance, Henzl and Morgenstern [5] concluded that bulk electrons determine the Kondo temperature \( T_K \) of Co/Ag(111) by intentionally depleting the spectral weight of the surface state at the Fermi level. The study of the Kondo resonance next to a monoatomic step edge led to the conclusion that the role of the surface states is marginal [21]. This is supported by the weak dependence of \( T_K \) of Co on noble-metal surfaces [31] with marked differences in the weight of their surface states relative to the bulk ones. On the contrary, the theoretically predicted [29,30] oscillations of the resonance line shape as a function of the tip lateral displacement on the order of the bulk electrons’ Fermi wavelength have not been observed [2,3,5]. In fact, the theoretical description by Merino et al. [32] cannot explain the distance-dependent data for Co/Cu(111) [3] without a major involvement of the surface states.

The seminal work on the quantum mirage of the Kondo resonance in the focus of elliptical resonators proves unambiguously a finite contribution of surfaces states [20]. Based on the relative intensity of \( dI/dV \) at both foci (one with a Co impurity and the other empty), a lower bound of 1/10 for the relative contribution of surface states has been estimated [33]. Moreover, the rather high \( T_K \sim 180 \) K of a Co porphyrin on \((\sqrt{3} \times \sqrt{3})\text{Ag-Si(111)}\), where bulk electron states are not present, indicates that a significant coupling between the surface states and magnetic impurity is possible [34]. In support of this, it was recently shown that \( dI/dV \) of Ag(111) oscillates as the resonance width of Co atoms near
step edges, quantum resonators, or another atom [35]. It is worth noting that, from the theoretical point of view, the Kondo effect is extremely sensitive to the hybridization channels between the impurity and the metal host electrons, which exhibit nontrivial dependencies on the k-space electronic structure of the surface and the actual adsorption geometry [36]. Thus, direct comparison of the Kondo resonance among different environments of the same adatom is physically inaccurate.

In this paper, we quantify the role of surface electron states in the Kondo effect of Co adatoms on Ag(111). We characterize their Kondo spectral features while varying just one single parameter of the problem: the surface-state contribution to the local density of states of the substrate \( \rho_s \). In Secs. II and III we develop the theoretical background on the basis of an Anderson model with SU(4) symmetry, which is consistent with the experimental spectroscopy as opposed to the SU(2) one [35]. Section IV is devoted to the experimental differential conductance \( dI/dV \) at position \( \mathbf{R} \) with \( (G_F) \) and without \( (G) \) Co impurity between the tip and the Ag(111) surface. The analysis of \( T_K(\mathbf{R}) \) and the amplitude of the Kondo resonance reveals that both magnitudes increase monotonically with \( G(\mathbf{R}) \). The theoretical calculation of the energy-resolved \( G \) for varying \( \rho_s \) is given in Sec. V, using both the noncrossing approximation (NCA) and poor man’s scaling (PMS). Finally, in Sec. VI the experimental and theoretical physical parameters are compared. We show that the coupling of the Co impurity state with extended states stemming from the surface state could be the dominant one and prove a threshold of at least one fourth of that of the bulk states.

II. SYMMETRY ANALYSIS

In analogy with other noble-metal surfaces [37], the Co atoms might occupy two inequivalent hollow positions on the Ag(111) surface, depending on whether the Co atoms lie above a Ag atom of the second layer or not (fcc/hcp). In both cases the symmetry point group is \( C_{3v} \). This group has three irreducible representations: \( A_1 \) and \( A_2 \) of dimension one and the two-dimensional representation \( E \). Disregarding spin for the moment, the Co 3d orbitals are split into one \( A_1 \) singlet and two \( E \) doublets, as sketched on the left side of Fig. 1. Choosing the coordinates in such a way that \( z \) is perpendicular to the surface and one of the Ag atoms nearest Co lies in the \( xz \) plane, the 3d orbital with symmetry \( 3z^2 - r^2 \) transforms as the \( A_1 \) representation, \( xz \) and \( yz \) transform like the \( E \) representation, and \( x^2 - y^2 \) transforms under the operations of \( C_{3v} \) in the same way as \( xz \) and \( yz \). Any Hamiltonian that respects the point group symmetry (without additional symmetry) mixes these two doublets, leading to bonding and antibonding states. In particular, the antibonding \( E \) states have the form

\[
|e_1\rangle = \alpha|xz\rangle + \beta|x^2 - y^2/2\rangle, \\
|e_2\rangle = \alpha|yz\rangle - \beta|xy\rangle.
\]

Additional adatoms on the surface break the \( C_{3v} \) symmetry, but this effect is small if these atoms are sufficiently far from the Co atom under study, as is the case in this work.

The Coulomb repulsion inside the 3d orbitals splits the energy necessary to add electrons in the same orbital. For example, let us call \( E_d \) the energy necessary to add the first electron in one of the antibonding \( E \) orbitals with any spin. This energy does not depend on the particular antibonding orbital chosen (\( e_1 \) or \( e_2 \)) or its spin. However, the extra energy cost to add the second electron is the Coulomb repulsion \( U \) between them. Similarly, the necessary energy to add the third or fourth electron is \( E_d + U \) plus the Coulomb repulsion with the previous ones. This is presented schematically on the right of Fig. 1. The actual position of the levels is more complex because it is modified by exchange and pair-hopping terms (see, for example, Ref. [38]), but they do not affect our treatment. For example, the ground state for occupancy 2 in the antibonding \( E \) is a triplet due to Hund’s rules. Instead, for occupancy 3 of theses states, the state is degenerate and is formed by two spin doublets with one hole in either \( e_1 \) or \( e_2 \). A similar splitting takes place for the bonding \( E \) and the \( A_1 \) states, which remain occupied in the neutral Co atom.

While symmetry alone cannot determine the ordering of the levels, the position of the observed Fano-Kondo dip \( \omega_K \) for positive energies of the order of the Kondo temperature \( T_K \) or larger [see, for instance, Fig. 2(b)] [39] points to an SU(4) Kondo system with occupancy close to 1, as we show below. This is consistent with the configuration 3d\(^7\) expected for a neutral Co atom, with four electrons occupying the bonding \( E \) orbitals, two in the \( A_1 \) orbital, and the remaining electron in one antibonding \( E \) orbital (Fig. 1). Other possibilities can be disregarded. For example, if both \( A_1 \) states were the highest in energy, putting two holes there and one in the antibonding \( E \) orbitals, the model presented in Sec. III still holds after an electron-hole transformation in the antibonding \( E \) orbitals, in which case the Kondo dip would be to the left of the Fermi energy (i.e., same differential conductance as in Fig. 2(b) but with the opposite bias sign). Assuming a 3d\(^8\) configuration, one has two possibilities to obtain a Kondo state: (i) two holes in the antibonding \( E \) states, except in this case the Kondo dip would be centered at the Fermi level [40], or (ii) one hole in an \( E \) state and one hole in an \( A_1 \) state. This is the case of Fe phthalocyanine on Au(111), which shows a two-stage Kondo effect with two features with different widths at the Fermi energy [25], completely different from our case. We have not discussed above combinations of holes in bonding and antibonding \( E \) orbitals because they are unlikely for Co.

Therefore, two channels are necessary to describe the system, and one-channel models [like the ordinary one-channel

*FIG. 1. Left: scheme of the splitting of the (one-particle) 3d orbitals under the point group \( C_{3v} \). Right: scheme of the splitting of the four antibonding states of symmetry \( E \) by the Coulomb repulsion. \( \varepsilon_F \) denotes the position of the Fermi energy compatible with the position of the observed Fano antiresonance.*
obtain a set of atoms spread on Ag(111) with the corresponding fit and Gaussian distribution profile (dashed line) for the SU(2) approximation \[41\]) the symmetry is SU(4) [larger than principle, a spin SU(2) times orbital SU(2) model. However, SU(2) Anderson or Kondo model] are ruled out. One has, in

QUANTIFYING THE LEADING ROLE OF THE SURFACE … PHYSICAL REVIEW B 97, 235442 (2018)

We assume constant densities of bulk states \(\rho_b\) extending in a wide range from \(-D\) to \(D\) and \(\rho_s\) extending from \(D_s\) to \(D_s (|D_s| < D)\). As we shall show, the fact that the surface band begins abruptly near the Fermi level at \(D_s = -67\) meV \[42\] (neglected in alternative treatments \[35\]) plays an essential role in the interpretation of the results. We also assume constant hybridizations \(V_b = V_k^b\) and \(V_s = V_k^s\). We believe that these assumptions are not crucial as long as the dependence of these parameters on energy is smooth in a range of a few times \(T_K\) around the Fermi energy. We define the couplings of the impurity state to bulk and surface state electrons as \(\Delta_s = \pi V_b |V_k^b|^2\) and \(\Delta_k = \pi V_s |V_k^s|^2\), respectively. Our work allows us to experimentally determine the ratio of these two quantities. \(E_d\) is the energy of the relevant impurity state.

We solve the model using two techniques: NCA (Sec. VA) \[11,43\] and PMS (Sec. VB) \[11,44\] on the effective Coulomb-Schrieffer model. These approaches are known to reproduce correctly the relevant energy scale \(T_K\) and its dependence on the Anderson parameters. In contrast to the numerical renormalization group in which the logarithmic discretization of the conduction band \[45,46\] broadens finite-energy features \[46,47\] and leads to inaccurate Kondo temperatures when a step in the conduction band is near the Fermi level, NCA correctly describes these features. For instance, the intensity and the width of the charge-transfer peak of the spectral density (the one near \(E_d\) were found \[48,49\] to be in agreement with other theoretical methods \[49–51\] and experiment \[52\]. The NCA works satisfactorily in cases in which the density of conduction states is not smooth \[53\], including, in particular, a step in the conduction band \[54\]. Furthermore, it has a natural extension to nonequilibrium conditions \[55\], and it is especially suitable for describing satellite peaks of the Kondo resonance, such as those observed in Ce systems \[56,57\], or away from zero-bias voltage in nonequilibrium transport \[58–61\]. Due to shortcomings of the approximation for finite \(U\) \[50,62,63\], we restrict our calculations to \(U \rightarrow \infty\), but this is not an essential approximation in our case \[41\].

The PMS is a perturbative approach that progressively integrates out a small portion of the conduction states lying at the bottom and top of the conduction bands, renormalizing the Kondo exchange coupling \(J_K\) \[11,44\].

### B. The STM tunneling conductance

The differential conductance \(dI/dV\) is proportional to the spectral density of the mixed state \(h_{i\sigma}(\mathbf{R}_t)\) at the position of the STM tip \(\mathbf{R}_t\) \[33\]:

\[
G(\epsilon) = dI/dV \propto \sum_{\sigma} \rho_{h\sigma}(\epsilon),
\]

\[
\rho_{h\sigma}(\omega) = \frac{1}{2\pi} \text{Im} \langle \tilde{G}_{h\sigma}(\omega - j\epsilon) - \tilde{G}_{h\sigma}(\omega + j\epsilon) \rangle,
\]

\[
h_{i\sigma}(\mathbf{R}_t) = \frac{1}{N} [s_{i\sigma}(\mathbf{R}_t) + p_b b_{i\sigma}(\mathbf{R}_t) + p_d d_{i\sigma}(\mathbf{R}_t) + \text{H.c.}],
\]

where \(V\) is the sample bias potential of the STM, \(\epsilon\) is the electron elementary charge, \(\tilde{G}_{h\sigma}(\omega) = \langle (h_{i\sigma}; h_{i\sigma}) \rangle_\omega\) is the Green’s function of \(h_{i\sigma}(\mathbf{R}_t)\), \(j\) is the imaginary unit, \(\epsilon\) is a positive infinitesimal, \(N\) is a normalization factor, \(p_b\) is the ratio of the tunneling matrix element between the STM tip and the

FIG. 2. (a) Representative raw \(dI/dV\) \([G_{k\sigma}(V)\), open circles\] showing the Kondo zero-bias feature at the center of a single Co atom and background estimation \([G_0(V)\), solid line\]. (b) Fit of the resulting \(g_k(V)\) to Eq. (7), yielding \(T_K = 56.1 \pm 0.9\) K, \(q = 0\), and \(\omega_K = 7.39 \pm 0.04\) meV. (c) Dispersion found in the Kondo resonance of a set of atoms spread on Ag(111) with the corresponding fit and \(T_K\) value. (d) Kondo temperature and (e) \(q\) factor statistics. Using a Gaussian distribution profile (dashed line) for the \(T_K\) histogram, we obtain \(T_K = 52.1 \pm 9.4\) K.

SU(2) Anderson or Kondo model] are ruled out. One has, in principle, a spin SU(2) times orbital SU(2) model. However, for large \(U\) (we take \(U \rightarrow \infty\), but this is not an essential approximation \[41\]) the symmetry is SU(4) [larger than SU(2) \(\times\) SU(2)], including orbital and spin degeneracies.

### III. MODEL AND FORMALISM

#### A. Hamiltonian

The Hamiltonian can be written as

\[
H = \sum_{k \sigma} \varepsilon_k s_{k \sigma}^\dagger s_{k \sigma} + \sum_{k \sigma} \varepsilon_k^b b_{k \sigma}^\dagger b_{k \sigma} + E_d \sum_\sigma d_{i\sigma}^\dagger d_{i\sigma} \\
+ U \sum_{i \sigma \sigma' j \sigma'} d_{i \sigma}^\dagger d_{j \sigma'} d_{j \sigma'}^\dagger + \sum_{k \sigma} V_k [d_{i \sigma}^\dagger s_{k \sigma} + \text{H.c.}] \\
+ \sum_{k \sigma} V_k^b [b_{k \sigma}^\dagger s_{k \sigma} + \text{H.c.}],
\]

where \(d_{i \sigma}^\dagger\) creates an electron in the antibonding orbital \(|e_i\rangle\) with spin \(\sigma\) and \(s_{k \sigma}^\dagger (b_{k \sigma}^\dagger)\) are creation operators for an electron in the \(k\)th surface (bulk) conduction eigenstate with symmetry \(i\) and spin \(\sigma\).
bulk states \( b_{i\sigma} \) and between the tip and surface states \( s_{i\sigma} \), and \( p_d \) is the analogous ratio for Co state \( d_{i\sigma}(\mathbf{R}) \) and surface states at the tip position. \( h_{i\sigma}(\mathbf{R}) \) represents the linear combination of surface, bulk, and Co 3d states probed by the tip.

Using equations of motion, \( \rho_{h\sigma}(\omega) \) can be related to the Green’s function for the \( d \) electrons \( \tilde{G}_{d\sigma}(\omega) = (\langle d_{i\sigma}; d_{i\sigma}^\dagger \rangle)_{\omega} \) and the unperturbed Green’s functions for conduction/bulk electrons \( \tilde{G}_{b\sigma}^0(\omega) \). In the absence of magnetic and symmetry-breaking fields we can drop the subscripts \( i\sigma \):

\[
\tilde{G}_h(\omega) = \tilde{G}_{d\sigma}^0(\omega) + p_d^2 \tilde{G}_{b\sigma}^0(\omega) + \Delta \tilde{G}_h(\omega). 
\]

\[
\Delta \tilde{G}_h(\omega) = 0 \text{ if the Co impurity is absent, and if not,}
\]

\[
\Delta \tilde{G}_h(\omega) = F^2(\omega)\tilde{G}_d(\omega),
\]

\[
F(\omega) = \nu_0 \tilde{G}_{d\sigma}^0(\omega) + p_b \nu_b \tilde{G}_{b\sigma}^0(\omega) + p_d,
\]

where

\[
\tilde{G}_{d\sigma}^0(R_1, R_2, \omega) = \rho_h \left[ \ln \left( \frac{\omega + D}{\omega - D} \right) \right],
\]

\[
\tilde{G}_{b\sigma}^0(R_1, R_2, \omega) = \rho_h \left[ \ln \left( \frac{\omega - D}{\omega + D} \right) \right].
\]

**IV. EXPERIMENTAL RESULTS**

Single Co atoms were deposited at low temperatures onto the Ag(111) surface \((T_x \sim 3 \text{ K})\) for an experimental temperature \( T = 1.1 \text{ K} \) cleaned by repeated cycles of sputtering with \( \text{Ar}^+ \) and annealing at 500 °C in UHV \((P_{\text{base}} \leq 1 \times 10^{-10} \text{ mbar})\). We use a lock-in amplifier to perform STS as a function of the applied sample bias \( V \). STS was acquired at constant height defined by the regulation set point \( V_0, I_0 \) on Ag(111) with rms modulation voltage \( V_{\text{mod}} \) and implemented in two modes: (i) single-point \( dI/dV \) spectroscopy \((V_{\text{mod}} = 0.5 \text{ mV}, V_0 = -100 \text{ mV}, I_0 = 42 \text{ pA})\) on top of Co atoms to obtain the energy-resolved \( G_K(\mathbf{R}) \) and (ii) \( dI/dV(x, y) \) mapping at the Fermi level \((V_{\text{mod}} = 1 \text{ mV}, V_0 = -100 \text{ mV}, I_0 = 200 \text{ pA})\) to measure the spatially resolved \( G(\mathbf{R}) \) of the Ag(111) inspected area after clearing it away from atoms by means of atomic manipulation (the typical set point for manipulation is \( V_0 = 3 \text{ mV}, I_0 = 40-70 \text{ nA} \)). The working temperature is \( T = 1.1 \text{ K} \) or \( T = 4.7 \text{ K} \), with the Kondo features of one atom in STS being identical at both temperatures.

Experimentally, the Kondo effect of isolated Co atoms on metals manifests as a Fano resonance \([2, 19, 31, 64]\) in the impurity \( G_K \) near the Fermi level. We describe this singularity as \( G_K = G_0 g_K \), where \( G_0(\mathbf{R}, \omega) \) is the convolution of the tip and the impurity density of states in the absence of Kondo screening and \( g_K(\mathbf{R}, \omega) \) contains the Fano function \( F(x, q) = (x + q)^2/1 + x^2 \) as follows:

\[
g_K(\mathbf{R}, \omega) = \left[ 1 - A_K(\mathbf{R}) \right] + A_K(\mathbf{R}) F \left( \frac{\omega - \omega_K}{\Gamma_0(\mathbf{R})/2} \right).
\]

Here \( \omega = eV \), \( \omega_K \) is the energy of the center of the Kondo resonance, \( q \) is the Fano asymmetry factor, \( A_K(\mathbf{R}) \) is the resonance amplitude when the atom sits at surface position \( \mathbf{R} \), and \( \Gamma_0(\mathbf{R}) \) is the resonance width, which is related to the Kondo temperature as \( 2k_B T_K \approx \Gamma_0 \) for \( T / T_K \rightarrow 0 \). Below \( T_K \) the spin of the extended states couples antiferromagnetically and screens the impurity spin, giving rise to the Kondo state \([10, 11]\). Figures 2(a) and 2(b) show the analysis of a Kondo resonance based on Eq. (7), which permits us to extract the parameters \( T_K(\mathbf{R}), A_K(\mathbf{R}), q, \) and \( \omega_K \) for each individual atom at position \( \mathbf{R} \).

We first analyze \( G_K \) of several Co atoms dispersed over the surface at their position right after the evaporation process (i.e., prior to any atom repositioning with the tip). Figures 2(c)–2(e) unveil a significant uncertainty in the parameters describing the Kondo resonance. The histograms elaborated from a set of 40 different atoms are shown in Figs. 2(d) and 2(e). \( T_K(\mathbf{R}) \) spans over a range of \( 28 \text{ K} \leq T_K \leq 95 \text{ K} \), with \( T_K \approx 52 \pm 9.4 \text{ K} \) being the most probable value. The most frequently found value for \( A_K \) and \( q \) is 0.2.

Apart from the hcp/fcc character of the hollow sites in a (111) surface termination, the adsorption geometry of disperse Co atoms is indistinguishable. We have confirmed that the Kondo parameters are the same in both sites except for a slightly lower amplitude \( A_K \) in one of them. Therefore, the different values obtained for \( T_K \) and \( q \) suggest a sensitivity to the density of surface states \( \rho_s(\mathbf{R}) \). Particularly, in Ag(111), the onset of the surface state lies in close proximity \((D_s = -67 \text{ meV})\) to the Fermi level \([42]\), leading to a Fermi wavelength \( \lambda_F \approx 8 \text{ nm} \) \([28]\), which is comparable to the distance between surface scatterers such as step edges, point impurities, and Co adatoms. This will produce interference patterns in \( \rho_s(\mathbf{R}) \) with a characteristic length scale of \( \lambda_F/2 \). We have shown elsewhere \([28]\) that \( \rho_s \) contributes strongly to the total density of states \( h_{i\sigma}(\mathbf{R}) \) probed by the tip. Therefore, it is natural to expect that changes in \( \rho_s(\mathbf{R}) \) will lead to the observed dispersion of \( T_K(\text{Co}/\text{Ag}(111)) \), through the hybridization of the Co 3d electrons with the surface states. This will become clear in Sec. VB, where an analytical expression for the dependence of \( T_K(\mathbf{R}) \) on \( \rho_s(\mathbf{R}) \) is presented.

To benchmark the correlation of \( T_K \) with the electronic properties of the substrate, we measure \( g_K \) [see Eq. (7)] over a Co atom at its natural adsorption site \( \mathbf{R} \) and subsequently at another position \( \mathbf{R}' \) far enough to have presumably a different \( \rho_s(\mathbf{R} - \mathbf{R}') \sim \lambda_F/2 \). In Fig. 3 we show \( g_K \) at each site in the absence of any tip change during the manipulation procedure. We find a strong variation of \( \Delta T_K = T_K(\mathbf{R}) - T_K(\mathbf{R}') \) being \( 24 \pm 4 \text{ K} \), well above the experimental uncertainty. This experiment shows unambiguously that the coupling strength between the localized spin and the Fermi gas of conduction state.
FIG. 4. $T_K$ and $A_K$ variations with $G(R)$. (a) STM image of Co/Ag(111) after Co deposition. (b) Co atoms are removed from the working area to avoid their influence on $G$. (c) Inset: constant-height $G(R) = dI/dV$ map taken at $V = 3 \text{ mV}$ ($I_0 = 200 \text{ pA}$, $V_0 = -100 \text{ mV}$, and $V_{\text{mod}} = 1 \text{ mV}$). (d) Co atom relocated at a certain position over the surface. (e) Experimental dependence of $T_K/(T_K)$ on the normalized local tunneling conductance $G/G_0$. (f) Experimental dependence of $A_K$ on $G/G_0$. In (e) and (f), the color code represents data sets taken with the same tip, while for the same color, the open and solid diamonds distinguish data sets at two different close working areas. All measurements were taken in constant-height mode at $T = 1.1 \text{ K}$ ($I_0 = 42 \text{ pA}$, $V_0 = -100 \text{ mV}$, and $V_{\text{mod}} = 0.5 \text{ mV}$). (g) Theoretical dependence of $T_K/(T_K)$ on $\rho_s/\rho_s^0$ for different values of $\Delta_s^0/\Delta_s$. The dashed lines are linear fits in the region $0 < T_K/(T_K) < 1.5$. The region enclosed within the dotted rectangle corresponds to the experimental parameter range.

electrons is strongly influenced by the local value of $\rho_s$ at each contact point.

Next, we evaluate more precisely this position-dependent Kondo effect through the analysis of $T_K$ and $A_K$ of Co atoms relocated in a region where $G(R)$ at Fermi level has previously been characterized (without Co atoms) in constant-height conditions. First, we clean out the atoms in the selected working area, as depicted in Figs. 4(a) and 4(b). Second, we take a $G(R)$ image of the differential conductance near the Fermi level ($0 < V < 3 \text{ mV}$), as shown in Fig. 4(c), whose maxima and minima reflect the characteristic interference pattern of the surface state. Afterwards, a single Co atom is moved across the inspected Ag(111) area [Fig. 4(d)], and we measure its energy spectrum $G_K(R)$ for each $R$ location. Note that this procedure is free of feedback artifacts and that the drift between consecutive images is corrected by always referring $R$ to a reference feature of the same image.

At the tip-sample distance at which the experiment is performed, the STM does not exhibit atomic resolution. Thus, $G(R)$ oscillations are contributed by only $\rho_s(R)$, owing to the interference pattern of scattered surface-state quasiparticles. In Figs. 4(e) and 4(f) we plot $T_K/(T_K)$ and $A_K$ as a function of $G/G_0$ for four different data sets gathered together, taken with different tips (symbols) at different working areas (color code). $G_0$ is defined as the tunneling conductance of an ideal surface without scattering sources. Experimentally, we determine $G_0$ to be the average differential conductance at Fermi level of a region much larger than $\lambda_F$, such as the one shown in Fig. 4(c). This normalization makes the analysis insensitive to the specific electronic structure of the tips used for the experiment. The resulting graphs display a monotonic increase of $T_K$ and $A_K$ with $G$, which implicitly provides evidence of the linear dependence of these parameters on $\rho_s$ within the experimental boundaries.

V. THEORETICAL RESULTS

In this section we present the theoretical results for the dependence of $T_K$ on the surface-state density $\rho_s$. For simplicity, from now on we choose the origin of energies to be $\varepsilon_F = 0$. We have taken $D_s = -67 \text{ meV}$ from experiment [21,28,66] and have chosen $D = 4 \text{ eV}$, $\rho_b = 0.135 \text{ eV}^{-1}$, $\rho_s = 0.0446 \text{ eV}^{-1}$ [28]. The results are rather insensitive to these parameters if the hybridizations are changed to fix the values of $\Delta_b$ and $\Delta_s$. For the energy of the occupied antibonding $E$ state with majority spin (see Fig. 1), we take $|E_d| \approx \Delta_{s,b}$ (in particular, $E_d = -2.2$). A different value would simply require a rescaling of $\Delta_{s,b}$.

Concerning the parameters entering Eq. (3), a previous comparison between experiment and theory on the action of Co resonators on the surface states [28] suggests that $p_b^2 \approx 1/16$. At first we took $|p_b| = 1/4$, but this implies a very large surface contribution ($\Delta^0_s/\Delta_b > 6$; see below). Furthermore, this estimation applies to a different tunneling barrier height [28], which may strongly alter the ratio $p_b$. Therefore, we think that it is better to be cautious and treat $p_b$ as an unknown parameter.
The shape of the resulting differential conductance $dI/dV$ is rather insensitive to the sign of $p_b$, but the intensity is smaller for $p_b < 0$. The parameter $p_d$ is determined by fitting the line shape. The line shape is rather insensitive to $p_b$ if $p_d$ is adjusted.

### A. Noncrossing approximation

1. Calculation of the Kondo temperature

To determine theoretically the value of the Kondo temperature $T_K$, we calculate the conductance through the magnetic impurity as a function of temperature $G_d(T)$ for a hypothetical case with $p_d \to \infty$ and look for the temperature such that $G_d(T_K) = \gamma_0/2$, where $\gamma_0$ is the ideal conductance of the system (reached for $T = 0$ and occupancy 1 of the impurity level). Alternative definitions of $T_K$ differ in the factor of the order of 1 [67], which is not relevant to us, as we shall show. We are interested in the dependence of $T_K$ with $\Delta_s$. In practice we take

$$G_d(T) = \gamma_0 \frac{\pi \Delta}{2} \int d\omega (-\frac{\partial f(\omega)}{\partial \omega}) \rho_d(\omega),$$

(8)

where $\Delta = \Delta_b + \Delta_s$, $\rho_d(\omega) = \sum_{\sigma} \rho_{d\sigma}(\omega)$ is the total impurity spectral density adding both orbitals $i$ and spins $\sigma$ and $f(\omega)$ is the Fermi function.

2. Fit of the experimental data

In Fig. 5 we show one experimental result for the differential conductance for which the resulting $T_K$ is very close to the average one ($T_K$) and the corresponding theoretical fit obtained at the experimental temperature $T = 4.7$ K. For the latter, we have assumed $\Delta_s = 0.27\Delta_b$, $p_b = 1.16$, which is consistent with the experimental slope of $T_K$ vs the tunneling conductance (see below) and adjusted $p_d$ to fit the experimental data. Very similar fits are obtained for larger values of $p_b$. The fit requires shifting the theoretical results by 4 meV to reach the experimental position of the dip $\omega_K = 7.7$ meV. The reason for this discrepancy might be due to details of the energy dependence of $\Delta_s$, which is particularly sensitive to the position of the adatoms [28] and which we have neglected in our approach.

Note that for the parameters in Fig. 5, the total width of the Fano dip is $\Gamma_0 = 8.71$ meV, while 2 times $T_K$ obtained from the definition based on Eq. (8) gives $2k_B T_K = 9.78$ meV. This ratio is approximately constant for the different parameters used here. Our Fano fit for this experimental curve gives $T_K = 56.1$ K $\sim 4.83$ meV. Therefore, we assume that this value is representative of the average Kondo temperature ($T_K$) observed in experiment. Note that the ratio $T_K/(\langle T_K \rangle)$ does not depend on the definition of $T_K$. We define $\rho^0_s$ and $\Delta^0_b = \pi \rho^0_s V^2$ as the values of the surface spectral density and $\Delta_s$ that lead to $T_K = \langle T_K \rangle$. $T_K$ depends mainly on $\Delta_s + \Delta_b$, and several ratios $\Delta_s/\Delta_b$ can lead to the same $T_K$.

In Fig. 4(g) we show the dependence of $T_K/(\langle T_K \rangle)$ on $\Delta_s/\Delta_b = \rho_s/\rho_b$ for several values of $R = \Delta^0_b/\Delta_s$. In good agreement with the experimental behavior of $T_K$ [Fig. 4(e)], we obtain a linear trend in the interval $0.5 < T_K/(\langle T_K \rangle) < 1.5$ with slope $B$. As expected, $B$ increases with increasing $R = \Delta^0_b/\Delta_s$. For larger $R$ the linear dependence weakens, and some curvature appears. The results for the slope $B$ for different ratios $R = \Delta^0_b/\Delta_s$ and the corresponding values of $p_b$ are listed in Table I.

| $R$ | $B$ | $C_b$ | $p_b$ |
|-----|-----|-------|------|
| 0.25 | 0.480 | 4.289 | 1.190 |
| 0.27 | 0.503 | 4.045 | 1.156 |
| 0.5 | 0.820 | 2.098 | 0.832 |
| 1 | 1.269 | 1.001 | 0.575 |
| 2 | 1.835 | 0.384 | 0.356 |
| 5 | 2.375 | 0.070 | 0.152 |

B. Poor man’s scaling

The PMS [11,44] for this SU(4) problem [or, in general, for SU(N) symmetry] up to second order in the Coqblin-Schrieffer interaction $J_K$ has the same form as for the SU(2) Kondo Hamiltonian treated previously [54], taking $NJK$ as the interaction constant. Then, borrowing previous results and taking the limit $U \to \infty$, we obtain the following analytical formula for the Kondo temperature as a function of $\Delta_b$ and $\Delta_s$:

$$T_K \simeq A|D_s|^{\eta} D^{1-\eta} \exp \left[ \frac{\pi E_d}{4(\Delta_b + \Delta_s)} \right],$$

(9)

$$\eta = \frac{\Delta_s}{(\Delta_b + \Delta_s)},$$

where for second order in $J_K$, $A = 1$. Higher-order corrections reduce $A$ and introduce logarithmic corrections. However, in our case, it is not possible to obtain an analytical formula like Eq. (9) if these corrections are included.

In Fig. 6 we plot this function for the same parameters as in Fig. 4(g), showing again a linear dependence in the relevant range of parameters, in agreement with experiment. We obtain

FIG. 5. Differential conductance as a function of voltage. Open circles: experimental $g_i$ [the same as Fig. 2(b)] without background. Red line: theory for $g_k$ circles: experimental $T$

TABLEI. Slope of $T_K/(\langle T_K \rangle)$ vs $\rho_s/\rho^0_b$, the corresponding $C_b$ value (see Sec. VI), and the coefficient of the bulk density of states in Eq. (5) for different ratios $R = \Delta^0_b/\Delta_s$. 

M. MORO-LAGARES et al. PHYSICAL REVIEW B 97, 235442 (2018)
for all positions as $G = C(\rho_s + p_b^0 \rho_b)$ [from Eqs. (3) and (4) with $\Delta G_b(\omega) = 0$]. Here $C$ and $\rho_b$ are constants. We write the differential conductance in the form $G = C\rho_s^0(\rho_s/\rho_s^0 + C_b)$, where $C_b = p_b^0 \rho_b/\rho_s^0$ is the relative weight of the bulk states in the tunneling conductance at reference point $T_K/(T_K) = 1$. $C_b$ is also a constant. Now, the theoretical analog of $G_0$ yields $G_0 = C_b^0(1 + C_b)$.

To compare the values of our theoretical slope $B$ of $T_K/(T_K)$ vs $\rho_s/\rho_s^0$ with the experimental slope $B_5 \simeq 2.54$ of $T_K/(T_K)$ vs $G/G_0$ obtained from the data in Fig. 4(e), we must take into account that

$$\frac{G}{G_0} = \frac{\rho_s/\rho_s^0 + C_b}{1 + C_b}. \quad (10)$$

It can be readily shown that $B_5 = (1 + C_b)B$. The fact that $\rho_s \geq 0$ for the minimum $G$ observed, $G_{min}/G_0 = 0.8$ (see Fig. 4), implies that $C_b/(1 + C_b) < 0.8$, which leads to the upper bound of $\sim 4$ for $C_b$. The corresponding theoretical value of $B = 0.503$ for the NCA method is obtained for $R = 0.27$ (Table I). Particularly, a lower bound of 0.1 was estimated for Co on Cu(111) based on the quantum mirage effect assuming $C_b = 1$ [33]. For a more realistic value of the minimum $\rho_s$ of about 60% of $\rho_s^0$ (the value for a surface without scattering sources), we obtain $B = 1.269$ and $R = 1$ (Table I), i.e., the same coupling of the impurity to the surface states as to the bulk ones.

VII. CONCLUSIONS

By combining STS and atomic lateral manipulation and applying a suitable Anderson Hamiltonian for the system, we have demonstrated that surface states have a relevant contribution in the formation of the Kondo state of Co/Ag(111). This result can be extended to other noble-metal surfaces and provides an important clue in the understanding of more complex correlated electron systems. The sensitivity of $T_K$ to the surface state suggests the possibility to tune the coupling strength between a magnetic impurity and its closest environment using confining nanostructures with size comparable to $\lambda_F$ [28]. In the case of Co/Ag(111) we propose a lower bound for the coupling of surface states to Co 3d states that is 27% of the one to bulk states. Furthermore, we show that a two-channel SU(4) Anderson model (considering both spin and orbital quantum numbers) is more appropriate to describe the Kondo effect than the one-channel SU(2) model. We also show that the proximity of the onset of the surface state to the Fermi level plays a crucial role in the observed approximately linear dependence of the Kondo temperature on the surface density of states.

ACKNOWLEDGMENTS

We thank N. Lorente and R. Robles for fruitful discussions. We acknowledge financial support provided by the Spanish MINECO (Grants No. MAT2013-46593-C6-3-P and No. MAT2016-78293-C6-6-R), as well as the Argentinian CONICET (PIP 112-201101-00832) and ANPCyT (PICT 2013-1045). M.M.-L., D.S., and M.R.I. acknowledge the use of Servicio de Apoyo a la Investigación-Universidad de Zaragoza.

TABLE II. Same as Table I calculated with PMS.

| $R$  | $B$   | $C_b$  | $\rho_b$ |
|------|-------|--------|----------|
| 0.25 | 0.414 | 5.135  | 1.302    |
| 0.27 | 0.445 | 4.709  | 1.247    |
| 0.5  | 0.713 | 2.562  | 0.920    |
| 1    | 1.070 | 1.374  | 0.674    |
| 2    | 1.465 | 0.734  | 0.492    |
| 5    | 1.878 | 0.352  | 0.341    |
The Kondo Problem to Heavy Fermions

A. C. Hewson, J. Kondo, Phys. Rev. 

V. Madhavan, W. Chen, T. Jamneala, M. F. Crommie, and N. S. Wingreen, Phys. Rev. B 64, 165412 (2001).

K. Andres, J. E. Graebner, and H. R. Ott, Phys. Rev. Lett. 88, 096804 (2002).

J. Heinrich, Science 319, 1066 (2008).

J. Li, W.-D. Schneider, R. Berndt, and B. Delley, Phys. Rev. Lett. 80, 2893 (1998).

M. Plihal and J. W. Gadzuk, Phys. Rev. B 63, 085404 (2001).

M. A. Schneider, P. Wühl, L. Diekühnöer, L. Vitali, G. Wittich, and K. Kern, Jpn. J. Appl. Phys. 44, 5328 (2005).

J. Merino and O. Gunnarsson, Phys. Rev. Lett. 93, 156601 (2004).

A. A. Aligia and A. M. Lobos, J. Phys.: Condens. Matter 17, S1095 (2005).

Q. Li, S. Yamazaki, T. Eguchi, H. Kim, S.-J. Kahng, J. F. Jia, Q. K. Xue, and Y. Hasegawa, Phys. Rev. B 80, 115431 (2009).

Q. L. Li, C. Zheng, R. Wang, B. F. Miao, R. X. Cao, L. Sun, D. Wu, Y. Z. Wu, S. C. Li, B. G. Wang et al., Phys. Rev. B 97, 035417 (2018).

C.-Y. Lin, A. H. Castro Neto, and B. A. Jones, Phys. Rev. B 71, 035417 (2005).

M. Ternes, C. P. Lutz, C. F. Hirjibehedin, F. J. Giessibl, and A. J. Heinrich, Science 319, 1066 (2008).

In our own experiments as well as those of Ref. [35] the dip in the differential conductance has a considerable shift to the right of the Fermi level. This is consistent with a Kondo effect with total $d$ occupancy $n_d$ near 1 for SU(4) symmetry but is not consistent with either $n_d \approx 1$ and SU(2) symmetry or $n_d \approx 2$ for the two-channel model. In these two cases, the Kondo peak is practically at the Fermi level in the Kondo limit [67]. In the Supplemental Material of Ref. [35] the Friedel sum rule [67] is inverted to estimate $0.4 < n_d < 0.66$ based on the simplest one-channel SU(2) Anderson model. This would indicate that the system is in the intermediate valence regime, instead of the Kondo one. The same analysis for the SU(4) case gives $0.8 < n_d < 1.3$, which is fully consistent with our SU(4) model in the Kondo regime.

M. Barral, S. Di Napoli, G. Blesio, P. Roura-Bas, A. Camjayi, L. Manuel, and A. Aligia, J. Chem. Phys. 146, 092315 (2017).

Calculations in a similar model indicate that the main effect of a finite $U$ is a shift to lower energies of the Kondo dip and an increase of its width that can be absorbed by renormalizing the (unknown) magnitude of both surface and bulk hybridizations by the same factor [69].

J. Li, W.-D. Schneider, and R. Berndt, Phys. Rev. B 56, 7656 (1997).

N. Bickers, Rev. Mod. Phys. 59, 845 (1987).

P. Anderson, J. Phys. C 3, 2436 (1970).

R. Žitko, Phys. Rev. B 84, 085142 (2011).

L. Vaugier, A. A. Aligia, and A. M. Lobos, Phys. Rev. B 76, 165112 (2007).

R. Žitko, Phys. Rev. B 84, 195116 (2011).

A. A. Aligia, P. Roura-Bas, and S. Florens, Phys. Rev. B 92, 035404 (2015).

J. Fernández, F. Lisandrini, P. Roura-Bas, C. Gazzola, and A. A. Aligia, Phys. Rev. B 97, 045144 (2018).

T. Pruschke and N. Grewe, Z. Phys. B 74, 439 (1989).

D. E. Logan, M. P. Eastwood, and M. A. Tusch, J. Phys.: Condens. Matter 10, 2673 (1998).

J. Könenmann, B. Kubala, J. König, and R. J. Haug, Phys. Rev. B 73, 033313 (2006).

J. Kroha and P. Wölfle, Acta Phys. Pol. B 29, 3781 (1998).

J. Fernández, A. A. Aligia, P. Roura-Bas, and J. A. Andrade, Phys. Rev. B 95, 045143 (2017).

N. S. Wingreen and Y. Meir, Phys. Rev. B 49, 11040 (1994).
[56] F. Reinert, D. Ehm, S. Schmidt, G. Nicolay, S. Hufner, J. Kroha, O. Trovarelli, and C. Geibel, Phys. Rev. Lett. 87, 106401 (2001).
[57] D. Ehm, S. Hufner, F. Reinert, J. Kroha, P. Wolflle, O. Stockert, C. Geibel, and H. v. Lohneysen, Phys. Rev. B 76, 045117 (2007).
[58] L. Tosi, P. Roura-Bas, and A. Aligia, J. Phys.: Condens. Matter 27, 335601 (2015).
[59] S. Di Napoli, P. Roura-Bas, A. Weichselbaum, and A. A. Aligia, Phys. Rev. B 90, 125149 (2014).
[60] P. Roura Bas and A. A. Aligia, Phys. Rev. B 80, 035308 (2009).
[61] P. Roura-Bas and A. A. Aligia, J. Phys.: Condens. Matter 22, 025602 (2009).
[62] K. Haule, S. Kirchner, J. Kroha, and P. Wollfe, Phys. Rev. B 64, 155111 (2001).

[63] L. Tosi, P. Roura-Bas, A. M. Llois, and A. O. Manuel, Phys. Rev. B 83, 073301 (2011).
[64] M. A. Schneider, L. Vitali, N. Knorr, and K. Kern, Phys. Rev. B 65, 121406 (2002).
[65] K. Nagaoka, T. Jamneala, M. Grobis, and M. F. Crommie, Phys. Rev. Lett. 88, 077205 (2002).
[66] M. Moro-Lagaers, Engineering Spin Structures at the Atomic Scale (Prensas de la Universidad de Zaragoza, Zaragoza, Spain, 2017).
[67] L. Tosi, P. Roura-Bas, A. Llois, and A. Aligia, Phys. B (Amsterdam, Neth.) 407, 3263 (2012).
[68] Y.-F. Yang, Z. Fisk, H.-O. Lee, J. Thompson, and D. Pines, Nature (London) 454, 611 (2008).
[69] J. Fernandez, A. A. Aligia, and A. M. Lobos, Europhys. Lett. 109, 37011 (2015).