Theory of Differential Conductance of Co on Cu(111) Including Co *s* and *d* Orbitals, and Surface and Bulk Cu States

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We revisit the theory of the Kondo effect observed by a scanning-tunneling microscope (STM) for transition-metal atoms (TMAs) on noble-metal surfaces, including *d* and *s* orbitals of the TMA, surface and bulk conduction states of the metal, and their hopping to the tip of the STM. Fitting the experimentally observed STM differential conductance for Co on Cu(111) including both the Kondo feature near the Fermi energy and the resonance below the surface band, we conclude that the STM senses mainly the Co *s* orbital and that the Kondo antiresonance is due to interference between states with electrons in the *s* orbital and a localized *d* orbital mediated by the conduction states.

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Introduction.—The detailed understanding of the interactions of a localized spin on a metallic surface with extended states are essential in promising quantum technologies, such as spintronics [1] where miniaturization reaches the atomic level. Several systems in which transition-metal atoms (TMAs), such as Co, Ti, or Cr, or molecules containing TMAs were deposited on noble-metal surfaces have been studied with STM [2–26]. The TMAs have a localized spin in the *d* shell, in which there are strong correlations, which are included in most theoretical treatments [27–34].

A ubiquitous phenomenon present in these systems is the Kondo effect. This effect is one of the most paradigmatic phenomena in condensed matter [35]. In its simplest form, it is characterized by the emergence of a many-body singlet at temperatures below the characteristic Kondo temperature T_K, formed by the localized spin and the spin of the conduction electrons near the Fermi level ϵ_F. As a consequence, the spectral density of the *d* electrons shows a resonance near ϵ_F. This resonance has the effect of pushing the conduction states away from ϵ_F and their spectral density shows a dip or Kondo antiresonance [27]. This effect is easily obtained using equations of motion for the Green's functions of the conduction electrons [29].

The observed differential conductance dI/dV has been usually interpreted using a phenomenological expression derived by Fano [36] for a noninteracting system, which takes into account the interference between localized and conduction states. According to the interpretation nowadays, the shape of dI/dV near zero voltage is determined by the ratio of the hoppings of the STM tip to the *d* and to the conduction electrons [29,34]. If the former dominates, the differential conductance represents the spectral density of the *d* electrons and a peak is observed. Instead, if the hopping of the STM tip to the conduction states dominates, a Fano-Kondo antiresonance is observed as a consequence of the corresponding dip in the conduction spectral density of states [27,29,34,37].

In contrast to other noble-metal surfaces, the (111) surfaces host a surface conduction band of Schockley states at ϵ_F [8,38,39]. The corresponding density of states is constant and begins nearly 70 (450) meV below ϵ_F for Ag (Cu or Au). Recent experiments by two different groups show the relevance of surface states in the Fano-Kondo antiresonance observed for Co on Ag(111) [23,24].

A crucial experiment that motivates our study is the observation in the differential conductance of a resonance below the bottom of the surface conduction band (RBBSCB), present when either magnetic or nonmagnetic TMAs are added on noble-metal surfaces [2,8,40]. A simple theoretical model indicates that dI/dV corresponds to the spectral density of a single atomic level, most likely an *s* one of the TMA, that hybridizes with surface and bulk states [8]. Because of the spatial extension of valence *s* states of TMAs, it is very reasonable to expect that they have a large hopping to the conduction states of the metal and also to the STM tip. In fact, the fit assumes implicitly that the hopping between the STM tip and the *s* orbital is larger than the corresponding ones between the STM tip and the conduction electrons. However, most of the previous studies of the Kondo line shape neglect the *s* states. Furthermore, while models exist that fit the observed dI/dV near ϵ_F (Kondo effect) and near the RBBSCB *separately*, a unified theory for both features is lacking so far. Our work closes this gap.

In this Letter, we provide a theory for the differential conductance dI/dV for Co on Cu(111) from voltage values below the onset of the surface band to positive values,

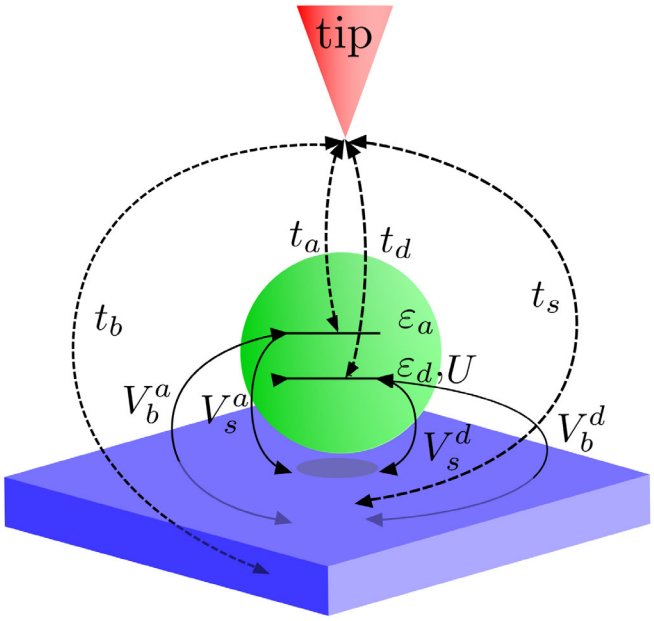

FIG. 1. Sketch of the system. The Co atom is described by a noninteracting level a representing an s orbital and a d level intraorbital Coulomb repulsion U. Both levels hop to the bulk and surface conduction states.

including those corresponding to the RBBSCB and the Kondo antiresonance [41]. Fitting both features together puts severe constraints on the hybridization between the d state and the extended conduction states and on the hopping between the tip and the different states. We find that the tip senses mostly the s state, which gathers information on the resonance below the onset of the surface band and the Kondo antiresonance through its hybridization with the extended conduction states.

Model and formalism.—A sketch of the system is represented in Fig. 1. The Hamiltonian is

$$\begin{aligned} H = &\sum_\sigma \varepsilon_a a_\sigma^\dagger a_\sigma + \sum_\sigma \varepsilon_d d_\sigma^\dagger d_\sigma + U d_\uparrow^\dagger d_\uparrow d_\downarrow^\dagger d_\downarrow \\ &+ \sum_{c=s,b}\sum_{k\sigma} \varepsilon_{ck} c_{k\sigma}^\dagger c_{k\sigma} + \sum_{c=s,b}\sum_{k\sigma} (V_c^a a_\sigma^\dagger c_{k\sigma} + \text{H.c.}), \\ &+ \sum_{c=s,b}\sum_{k\sigma} (V_c^d d_\sigma^\dagger c_{k\sigma} + \text{H.c.}). \end{aligned} \tag{1}$$

The first three terms represent an s (denoted by a) and a d orbital of the Co atom, and the interaction between two d electrons. The fourth term describes the two conduction bands corresponding to bulk (b) and surface (s) extended states. The remaining terms describe the hybridization between Co and conduction states. An analysis based on symmetry indicates that the d orbital corresponds to the $3z^2 - r^2$ one [41] and that the s orbital has an admixture with the p_z one [33,41] which lies at higher energy.

A model containing s and d orbitals has been studied in Ref. [33], but the surface states were not included, and therefore the RBBSCB cannot be described. In addition, the authors obtained a peak instead of a dip for the feature near $V = 0$.

In the tunneling regime (as opposed to the contact regime [42,43]) of the STM, the differential conductance dI/dV is proportional to the spectral density of a state $h_\sigma^\dagger$ which consists of a linear combination of all local and extended states with a coefficient proportional to the corresponding hopping to the tip [29]:

$$\frac{dI(V)}{dV} \propto \rho_{h\sigma}(eV) = -\frac{1}{\pi}\text{Im}\langle\langle h_\sigma; h_\sigma^\dagger\rangle\rangle_{\omega=eV}, \tag{2}$$

Assuming a local hopping of the tip with the different states, the state $h_\sigma^\dagger$ for spin σ can be written as

$$h_\sigma^\dagger = t_a a_\sigma^\dagger + t_d d_\sigma^\dagger + t_s s_\sigma^\dagger(r_t) + t_b b_\sigma^\dagger(r_t), \tag{3}$$

where $c_\sigma(r_t)$ denotes the operator of (surface $c = s$ or bulk $c = b$) conduction states at the Wannier function below the tip and t_μ ($\mu = a, d, s$ or b) are proportional to the hopping between the tip and the different states.

Alternatively Eq. (3) can be derived from the formalism of Meir and Wingreen [44] assuming that the presence of the STM tip does not disturb the rest of the system and that the whole potential difference falls between the tip and the rest of the system [45].

We assume that the tip is located just above the impurity, see Fig. 1 ($r_t = r_{\text{imp}}$, denoting r_t and r_{imp} the position of the tip and the adatom on the surface, respectively). A generalization to $r_t \neq r_{\text{imp}}$ is straightforward [29]. The electrons of the tip can hop to both TMA levels and the conduction states as sketched in Fig. 1. Using the equations of motion, we can write the Green's function of the mixed state as

$$\langle\langle h_\sigma; h_\sigma^\dagger\rangle\rangle_\omega = \sum_c t_c^2 G_c^0(\omega) + F(\omega), \tag{4}$$

with

$$F(\omega) = \sum_\xi \tilde{t}_\xi^2 \langle\langle \xi_\sigma; \xi_\sigma^\dagger\rangle\rangle_\omega + 2\tilde{t}_d\tilde{t}_a\langle\langle d_\sigma; a_\sigma^\dagger\rangle\rangle_\omega, \tag{5}$$

where $\xi = a$ or d denotes the TMA orbitals and $\tilde{t}_\xi$ is defined as

$$\tilde{t}_\xi = t_\xi + \sum_c t_c G_c^0(\omega) V_c^\xi. \tag{6}$$

Outline of the calculations.—Our first step was to map the Hamiltonian Eq. (1) into a simpler Anderson model which hybridizes the localized d state with a single band of noninteracting states which includes the surface and bulk

conduction states as well as the s state. The details are contained in Sec. II of the Supplemental Material (SM) [46]. This noninteracting band has energy dependent density of states and hybridization with the d state.

This model is solved using the numerical renormalization group [47], from which we obtain the Green's function of the d states $\langle\langle d_\sigma; d_\sigma^\dagger \rangle\rangle_\omega$ with high accuracy.

Finally, using equations of motion, the Green's function entering the differential conductance [Eqs. (2)–(6)] can be exactly expressed in terms of $\langle\langle d_\sigma; d_\sigma^\dagger \rangle\rangle_\omega$, as explained in the SM [46].

Parameters of the Hamiltonian.—We take constant hybridizations and unperturbed densities of conduction states. The surface density of states per spin in the absence of the Co atom, corresponds to two-dimensional free electrons and is known to be constant [8,38]. We include lifetime effects in the lower band edge, following the experimental adjustment made by Limot *et al.* [8]. Details are in the SM [46]. Since the Fermi wavelength of surface electrons is much larger than the atomic size, the corresponding hybridizations should have very weak k dependence. The energy dependence of the unperturbed bulk density of states and the hybridizations with Co s and d states is expected to be weak in the range of energies of interest and does not affect our main conclusions.

We choose the origin of energies at $\epsilon_F = 0$. We have taken $\varepsilon_a = 0.33$ eV, $V_b^a = -1.41$ eV, and $V_s^a = -1.46$ eV from Ref. [8] and $\varepsilon_d = -0.8$ eV from Ref. [29]. The results near the Kondo feature are rather insensitive to ε_d if the ratios Δ_c^d/ε_d are kept constant, where $\Delta_c^\xi = \pi\rho_c(V_c^\xi)^2$, $c = b$ or s, and $\xi = d$ or a. From the splitting between the positions of the majority and minority peaks in the spectral density of Co states on Ag(111) obtained by first-principles calculations, $U = 1.6$ eV is estimated [48] [we expect a similar U for Co on Cu(111)]. The width of the Kondo feature is basically determined by $\Delta_b^d + \Delta_s^d$, which acts as a constraint on the parameters. The amplitude of the observed Fano antiresonance at ϵ_F decreases with decreasing $R = \Delta_s^d/\Delta_b^d$, and too small R is incompatible with the experiment. Details are in the SM [46]. Taking into account recent studies in similar systems [24] we have taken $R = 0.5$. If both the RBBSCB and the Kondo dip were measured in a single experiment one could quantitatively determine R.

In contrast to previous works in which only the Kondo feature was fitted, we find that the relative *sign* of the different V_c^ξ plays a mayor role. Because of the symmetry of the s orbitals that form the conduction band and the Co s orbital, one expects that $V_c^a < 0$. Instead, the sign of V_c^d is difficult to predict on general physical grounds. Our results indicate $V_b^d < 0$, $V_s^d > 0$.

Results.—We discuss first the general features of the spectral densities of states $\rho_d(\omega)$ and $\rho_a(\omega)$ for a given spin and then present our fits for the observed differential conductance. The spectral density for d electrons, shown in Fig. 2 has the expected features for the impurity Anderson model, in particular a resonance at ϵ_F, and in addition a small step at the onset of the surface band.

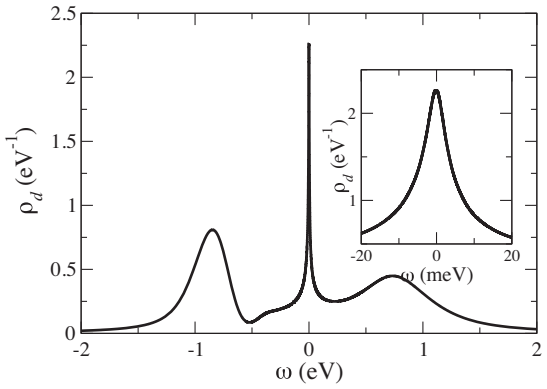

FIG. 2. Spectral density for a given spin of the d-orbital as a function of energy for $\varepsilon_d = -0.8$ eV, $U = 1.6$ eV, $\varepsilon_a = 0, 33$ eV, $V_b^d = -0.50$ eV, $V_s^d = 0.62$ eV, $V_b^a = -1.41$ eV, and $V_s^a = -1.46$ eV at $T = 4$ K. The inset shows details of the Kondo peak near $\omega = 0$.

The spectral density for the s state is displayed in Fig. 3. The resonance below the onset of the surface band is clearly seen. As a first approximation, this resonance can be understood as a result of the hybridization of the s state with a surface bound state, broadened by the hybridization with bulk conduction states. This point is discussed further below.

In addition, there is also a peak at ϵ_F. This is due to an effective hybridization between Co s and d orbitals mediated by the bulk and surface conduction bands.

In Fig. 4, we compare the observed differential conductance dI/dV for Co on Cu(111) [8,37] with our theory given by Eq. (2). In spite of the fact that the spectral density of both s and d electrons has a peak at ϵ_F, dI/dV has a dip. This is due to the fact that the imaginary part of the crossed

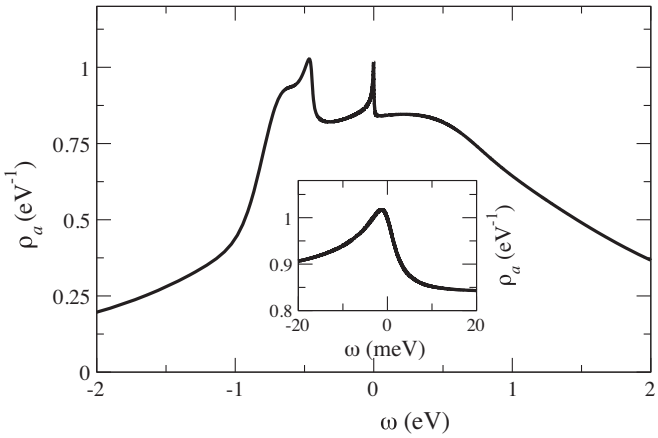

FIG. 3. Spectral density for a given spin of the Co s orbital as a function of energy for the same parameters as Fig. 2. The inset shows details of the peak near $\omega = 0$.

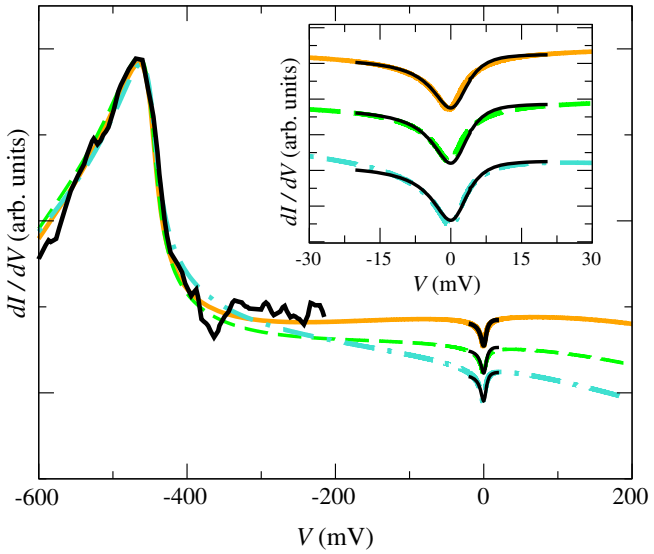

FIG. 4. Differential conductance as a function of voltage. Black solid line: experimental dI/dV for Co/Cu(111). Orange solid line: $t_a = -0.978$, $t_d = -0.175$, $t_s = -0.1$, and $t_b = -0.04$. Green dashed line: $t_a = -0.959$, $t_d = -0.192$, $t_s = -0.2$, and $t_b = -0.08$. Blue dashed-dot line: $t_a = -0.925$, $t_d = -0.185$, $t_s = -0.31$, and $t_b = -0.12$. The inset displays the Kondo dip.

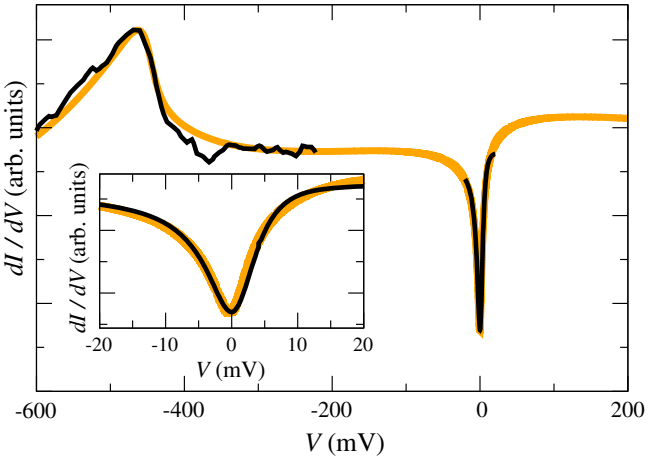

FIG. 5. Same as Fig. 4 for $V_s^d = -1.36$ eV, $t_a = -0.67$, $t_d = -0.24$, $t_s = -0.67$, and $t_b = 0.20$. The inset shows the Kondo dip at low energies.

Green's function $\langle\langle d_\sigma; a_\sigma^\dagger \rangle\rangle_\omega$ is negative and dominates the behavior of dI/dV through the last term of Eq. (5) [46].

Two different experiments were performed for the regions near −0.5 V and 0. Then, the corresponding experimental results were multiplied by different factors. Beyond this uncertainty, the comparison between theory and experiment is excellent. The locations of the RBBSCB near −0.5 V, and the Kondo dip at zero bias are well reproduced as well as the width of them. The parameters for the adjustment are normalized in such a way that $t_a^2 + t_a^2 + t_s^2 + t_b^2 = 1$. For small values of t_a, the RBBSCB cannot be fitted. An analysis of the variation of the fit with different parameters is in Sec. III of the SM [46]. The fit is practically unchanged along a line in a three-dimensional space of the independent t_i as long as $0.925 \leq |t_a| \leq 0.978$. For smaller values of $|t_a|$, the fit deteriorates rapidly near −300 and −15 V and the magnitude of the slope between these voltages increases.

We note that the presence of the s state is essential to reproduce the experimentally observed dI/dV. While it is known that any attractive scattering potential leads to a bound state below a two-dimensional band, the shape of the resulting bound state in the spectral density of the surface states for a local scattering without including the s state (Fig. 8 of Ref. [49]) is different from that observed. In Fig. S7 of the SM [46] we compare the contribution of the s state and the surface conduction band to dI/dV. They are very different and only the former agrees with experiment.

In Fig. 5 we show the best fit for a negative value of V_s^d. For all negative V_s^d, the magnitude of the Kondo dip is significantly larger than that of the feature below the surface band, which seems very unlikely in comparison with the experiments for Co on noble-metal surfaces [2,8].

Discussion.—The fact that the dominant hopping between the STM tip and the TMA and conduction states corresponds to the s state ($|t_a| \gg |t_d|, |t_s|, |t_b|$) is one of the main results of this Letter. Although this is expected from the spatial extension of the Co 4s orbital and its position near to the tip (see Fig. 1), this fact has been overlooked so far in the description of the Kondo antiresonance. A single measurement of dI/dV in the whole voltage range combined with our theory might quantify the relative importance of the surface states in the Kondo effect.

Other experimental observations are also consistent with our theory. t_a is expected to be dominated by hopping between different s orbitals, which has a $1/r$ distance dependence [50]. Hence, when t_a dominates, following Eqs. (4)–(6), a $1/|r_t - r_{\rm imp}|^2$ distance dependence of the differential conductance is expected, when the tip is separated from the Co atom, as observed by Knorr *et al.* [6]. These authors have ascribed this dependence to a minor role of the surface states in the formation of the Kondo resonance, but this interpretation contradicts recent experiments [23,24]. If in our results we turn off the surface states ($V_s^d = t_s = 0$), we obtain a peak instead of a dip at zero bias, in agreement with previous theoretical works [32,33]. This is what is observed for Co on Cu(100) [7,10–12,14], a surface that has not Shockley surface states.

We expect that our results will be relevant for the interpretation of other STM experiments involving transition metal adatoms and molecules containing magnetic transition-metal atoms on metallic surfaces.

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