Kondo Effect and Surface-State Electrons

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We have used low temperature scanning tunneling spectroscopy and atomic manipulation to study the role of surface-state electrons in the Kondo effect of an isolated cobalt atom adsorbed on Ag(111). We show that the observed Kondo signature remains unchanged in close proximity of a monoatomic step, where the local density of states of the surface-state electrons is strongly perturbed. This result indicates a minor role for surface-state electrons in the Kondo effect of cobalt, compared to bulk electrons. A possible explanation for our findings is presented.

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Recently, scanning tunneling microscopy (STM) has been used to investigate the electronic properties of single magnetic impurities on the surface of metals, opening a new avenue of research into the Kondo effect [1, 2]. The Kondo effect occurs when a magnetic impurity in a metal couples to surrounding conduction electrons. This coupling, which involves spin-flip scattering events on the site of the impurity, causes conduction electrons to form a correlated ground state that screens the magnetic moment of the impurity at temperatures below a characteristic Kondo temperature ($T_K$). It also leads to a narrow resonance in the local density of states (LDOS) of the impurity at the Fermi energy ($E_F$), which is detected in STM and, in particular, in scanning tunneling spectroscopy (STS).

Owing to the atomic resolution in space and the better than meV resolution in energy, STM and STS can perform local investigations of the Kondo effect, directly at the adsorption site of single magnetic atoms on the surface of metals. However, for a comparison to bulk measurements, differences in the bulk and in the surface electronic structures must be taken into account. For instance, well known bulk Kondo systems yield Kondo temperatures substantially higher than the ones reported by STM [2, 4, 6]. Furthermore, most STM and STS measurements have been performed on (111) facets of noble metals, where bulk electrons co-exist with Shockley surface-state electrons, which form a quasi-two-dimensional electron gas trapped between the surface barrier potential and a band gap in the crystal.

So far, there still is a lack of experimental and theoretical data concerning the role of the surface-state electrons in the Kondo effect. In this brief report we specifically focus on this topic. We report a STM and a STS study for cobalt adatoms on Ag(111), where the combination of controlled cobalt manipulation over the surface and tunneling-spectroscopy of cobalt adatoms enables us to tune the LDOS of the surface-state electrons and thus probe its influence on the Kondo temperature of Co/Ag(111). We also provide a possible scenario to interpret our data, which, we hope, will trigger further theoretical studies.

The measurements were performed in a home-built ultrahigh vacuum STM at a working temperature of $T = 4.6$ K and the Ag(111) surface was cleaned by Ar+ sputter/anneal cycles. Single cobalt atoms were evaporated onto the cold Ag substrate by heating a degassed cobalt wire (> 99.99%) wound around a pure W wire (> 99.95%). The evaporation, through an opening of the He shield of the cryostat, yielded a coverage of $3 \times 10^{-3}$ ML. No appreciable increase of other impurities was detected. After the evaporation, the thermalization of Ag(111) to 4.6 K ensured a negligible thermal diffusion of cobalt adatoms within measurement times. Spectra of the differential conductance of the tunneling junction, $dI/dV(V)$, were recorded via lock-in detection (AC modulation was 1 mV (rms) in amplitude and ~10 kHz in frequency), where $V$ is the sample bias measured with respect to the tip. The images and the spectra were recorded with a etched tungsten tip; the tip was further treated in situ by soft indentations into the Ag(111) surface, until the cobalt adatoms were imaged spherically (Fig. 1), and the $dI/dV$ had no structure near the zero bias voltage, i.e. the Fermi energy. The cobalt adatoms have then a Gaussian-like profile ~ 0.7 Å high with an apparent diameter of ~ 6 Å (full width at half maximum).

A typical $dI/dV$ spectrum acquired at the center of a cobalt adatom is presented in Fig. 2. The dip in the LDOS near $E_F$ is the signature in STS of the Kondo effect of Co/Ag(111). When the tip is moved laterally off the cobalt adatom, the dip continuously decreases in amplitude and vanishes at $\approx 8$ Å away from the center of the cobalt atom; at a distance of $\gtrsim 50$ Å, the $dI/dV$ spectrum of the Ag(111) surface-state is recovered (Fig. 2a). A similar dip at $E_F$ has previously been observed in STS for other Kondo systems like Ce/Ag(111) and Co/Cu(111) in the asymmetric line shape observed for Co/Au(111), Ti/Ag(100) and Co/Cu(100) in contrast to the asymmetric line shape observed for Co/Au(111), Ti/Ag(100) and Co/Cu(100) [2, 5, 6]. The $dI/dV$ spectrum can be understood following the pioneering framework by Fano [3]. When $T \ll T_K$, spin-flip processes are frozen out and the
4.6 K, a Fano parameter $q$.

The Fano fits on various cobalt spectra yielded the following information concerning the Kondo effect for Co/Ag(111).

$dI/dV$ produces a symmetric or an asymmetric line in the spectrum, depending on the relative weight of the two channels. Modelling of the dip of Fig. 2a with a Fano line allows then to extract from the spectrum. Following the expression of Ref. 10, the cobalt adatom is trapped below the tip and gently dragged to a desired location on the surface – in Fig. 3b, at 8 Å from a monoatomic step of Ag(111).

Figure 3 presents $dI/dV$ data acquired over a cobalt adatom positioned below the step of Fig. 3a, at 8 Å from a monoatomic step of Ag(111). Figure 3a presents $dI/dV$ with respect to the bulk LDOS ($\rho_b$) is strongly perturbed. Figure 3b illustrates a typical manipulation procedure we performed. By placing the STM tip over a cobalt adatom and by applying $I = 2.8$ nA and $V = 2.8$ V to the tunneling junction (Fig. 3a), the cobalt adatom is trapped below the tip and gently dragged to a desired location on the surface – in Fig. 3b, at 8 Å from a monoatomic step of Ag(111). Figure 3a presents $dI/dV$ data acquired over a cobalt adatom positioned below the step of Fig. 3a at distances $r$ from the step edge of 8, 13 and 24 Å. The Fano fits to the three spectra do not reveal any appreciable change in the resonance, indicating that $T_K$ is constant with $r$. Near a step, however, $\rho_s$ is strongly perturbed at $E_F$ because of the back-scattering of the surface state by the step – contrary to the bulk LDOS ($\rho_b$). Neglecting thermal broadening, the spatial variation of $\rho_s(E_F)$ is approximately described by a Bessel function $1 - J_0(2k_Fr)$, where $k_F = 0.084$ Å$^{-1}$ for Ag(111). The dependency of $\rho_s(E_F)$ on $r$ is presented in Fig. 4b where we have also indicated the positions where the spectra of Fig. 4a were recorded. As shown, when moving from $r = 24$ Å to $r = 8$ Å, $\rho_s(E_F)$ decreases by more than a factor three, to be compared to the constant value of $T_K$ observed for Co/Ag(111) at a Ag(111) step. The only significant spectroscopic change we observe in the Kondo effect of Co/Ag(111) is for artificially fabricated cobalt dimers, where, in agreement with the findings of Ref. 12, an abrupt disappearance of the Kondo resonance occurs.

Kondo many-body problem reduces to a single-particle resonance near $E_F$ of width $2k_B T_K$, which, in principle, should be detected in a $dI/dV$ spectrum. However, tunneling from the tip into the Kondo resonance occurs through two channels: a direct one, and an indirect one via the $sp$ substrate conduction band locally hybridized with the cobalt $d$ levels (which are giving rise to the magnetic moment of the cobalt atom). The interference between the two channels – known as Fano interference – produces a symmetric or an asymmetric line in the $dI/dV$ spectrum, depending on the relative weight of the two channels. Modelling of the dip of Fig. 2a, with a Fano line, allows then to extract from the $dI/dV$ spectrum information concerning the Kondo effect for Co/Ag(111). The Fano fits to various cobalt spectra yielded the following results: from the line width we extract a temperature $T_K = 83(10)$ K higher than our working temperature of 4.6 K, a Fano parameter $q = 0.0(1)$ – indicating that the predominant tunneling channel is through the $sp$ band – and a shift of the resonance to 5.8(4) meV above $E_F$.

The reported values are in good agreement with a previous STS study of Co/Ag(111), where a temperature of $T_K = 92(6)$ K was found by Schneider et al. [11].

Figures 2 and 3 illustrate the main experimental findings of this report. To explore the role played by the Ag(111) surface-state electrons in the Kondo effect of Co/Ag(111), we combined manipulation and spectroscopy experiments to probe how the Kondo effect of Co/Ag(111) is affected in close proximity of a monoatomic step of Ag(111) where the surface-state LDOS ($\rho_s$) is strongly perturbed.

FIG. 1: Constant current STM image of an isolated cobalt adatom on Ag(111) (11 × 11 nm$^2$, $I = 0.5$ nA, $V = 100$ mV). Also visible, the scattering of the Ag(111) surface state by the adatom.

FIG. 2: a) $dI/dV$ spectrum taken at the center of a cobalt adatom ($I = 0.5$ nA, $V = 100$ mV). The spectrum is an average of 10 single spectra from varying cobalt adatoms and tips. Solid line: Fano fit following the expression of Ref. 10. b) $dI/dV$ spectrum taken over a bare terrace of Ag(111) ($I = 0.5$ nA, $V = 100$ mV). The onset at −67 meV corresponds to the energy of the low band edge of the Ag(111) surface-state. After the onset, the contribution of the surface LDOS to the $dI/dV$ with respect to the bulk LDOS is $\rho_s/\rho_b \approx 2$.

FIG. 3: Cobalt adatom near a monoatomic step of Ag(111) (17 × 17 nm$^2$, $I = 0.5$ nA, $V = 10$ mV). a) Prior, and, b) After manipulation.
First, as seen in Eq. 1, the Kondo temperature of a magnetic scatterer depends exponentially on $J\rho$. Since experimentally $T_K$ is found to be insensitive to a variation of $\rho_s$ by a factor of three, we conclude that the Kondo effect of cobalt atoms adsorbed on Ag(111) involves mainly bulk electrons: $J\rho \approx J_b\rho_b$. This conclusion agrees with those of Refs. [3] where the Kondo temperature of the Co/Cu(111) and Co/Cu(100) systems was shown to vary with the number of next nearest Cu neighbors ($n$) of the cobalt atom, hence with $\rho_b \sim n$.

Next, we focus more specifically on the surface-state electron coupling $J_s$. At the tip-surface distances where usual $dI/dV$ spectra are acquired ($\sim 10$ Å over the surface), about 2/3 of the current into the Ag(111) surface is due to tunneling into the surface-state LDOS (see Fig. 2b), and in particular $\rho_s/\rho_b \approx 2$ at $E_F$. Assuming that this ratio between the two LDOS holds also at the cobalt site, i.e. that $\rho_s \sim \rho_b$ at the impurity site, the feeble contribution of the surface-state electrons to the Kondo effect is to be found then in a weaker coupling to the magnetic moment of the cobalt atom compared to bulk electrons: $J_s \ll J_b$. While $J_s$ is small, it is clearly non-zero, as demonstrated by Manoharan et al. in their quantum mirage experiment [4], where they exploited the scattering of the Cu(111) surface-state electrons in an elliptical quantum corral to project the Fano line of a cobalt adatom in one focus to the other empty focus, about 80 Å away. However, only ellipses of specific dimensions will have a sufficient surface-state electron amplitude at the focal adatom to yield a detectable Kondo signal at the opposite focus [4, 15], in agreement with our finding of a minor involvement of surface-state electrons in the surface Kondo effect.

In conclusion, we have studied the Kondo effect of cobalt atoms adsorbed on the surface of Ag(111) by STM and by STS. The Kondo signature in the $dI/dV$ of Co/Ag(111) is a damped Fano resonance near $E_F$ from which is extracted a Kondo temperature of $T_K = 83(10)$ K. A combination of cobalt-manipulation and tunneling spectroscopy, suggests, on an experimental basis, that the role of surface-state electrons in the Kondo effect of Co/Ag(111) is minor, possibly because of a weaker coupling $J_s$ compared to the one of the bulk electrons. This appears to be a general property of Kondo systems and, we hope, will trigger further theoretical studies for a quantitative understanding of our experimental data.

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