Temperature Dependence of a Single Kondo Impurity

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Recent advances in scanning tunneling microscopy have allowed the observation of the Kondo effect for individual magnetic atoms. One hallmark of the Kondo effect is a strong temperature-induced broadening of the Kondo resonance. In order to test this prediction for individual impurities, we have investigated the temperature dependent electronic structure of isolated Ti atoms on Ag(100). We find that the Kondo resonance is strongly broadened in the temperature range $T = 6.8$ K to $T = 49.0$ K. These results are in good agreement with theoretical predictions for Kondo impurities in the Fermi liquid regime, and confirm the role of electron-electron scattering as the main thermal broadening mechanism.

When magnetic structures are reduced to atomic length scales and contacted to a metal, the coupling between spin and conduction degrees of freedom leads to the Kondo effect [1]. The Kondo effect is characterized by the formation of a many-body electronic ground state that screens the local magnetic moment of an impurity and produces a narrow electronic resonance at the Fermi level (the "Kondo resonance" [1,2]). Important characteristics of the Kondo effect are the splitting of the Kondo resonance under an applied magnetic field and the broadening and reduction of the Kondo resonance at increased temperatures [3–7]. Recently, scanning tunneling microscope (STM) experiments have probed single magnetic impurity systems, and the Kondo resonance has been observed for individual atoms [8–10]. Although these measurements can be explained by Kondo physics, the critical test of temperature dependence has yet to be reported for individual impurities.

Here we report an experimental study of the temperature dependence of the Kondo resonance for an individual magnetic impurity. Ti atoms resting on a Ag(100) surface were spectroscopically probed using a variable temperature STM over the temperature range $T = 7$–49 K. Thermal deconvolution of the resulting spectra reveals that the Ti Kondo resonance broadens quadratically at low temperature and follows a simple functional dependence that is well explained by the Fermi liquid treatment of the Kondo effect. These results reveal the important role of electron-electron scattering in determining the electronic structure of surface magnetic impurities.

The experiments were performed using a homebuilt STM contained in ultrahigh vacuum (UHV) and cooled by a liquid He bath via exchange gas. The single-crystal Ag(100) substrate was cleaned in UHV by repeated cycles of Ar-ion sputtering and annealing. The clean Ag(100) surface was then cooled to 7 K and dosed in UHV with a Ti e-beam evaporator source. After evaporation, the sample and STM were both warmed to the target temperatures before performing local spectroscopic measurements (temperature was measured using diodes placed at two points near the sample). dI/dV spectra were measured through lock-in detection of the ac tunnel current driven by a 450 Hz, 1 mV (rms) signal added to the junction bias under "open-loop" conditions.

Figure 1 shows a constant-current topograph (400 Å × 400 Å) of a typical Ag(100) surface after deposition of $\sim$0.002 monolayer of Ti at $T = 7$ K. Each protrusion seen here corresponds to a single Ti atom having an apparent height of 2.0 Å. The combination of Ti and Ag(100) was used in this study for several reasons. We chose the (100) surface of an fcc crystal because it is more highly corrugated than other low index surfaces, thus helping to impede adatom diffusion at increased temperatures. One reason for choosing Ag as the substrate material is that Ti is predicted to have a robust magnetic moment ($2\mu_B$) on Ag(100) [11]. Ti was also chosen because it was found to have a more pronounced Kondo resonance on Ag(100) than any other $3d$ transition metal element tested on this surface (such as V, Cr, Mn, Fe, Co, and Ni).
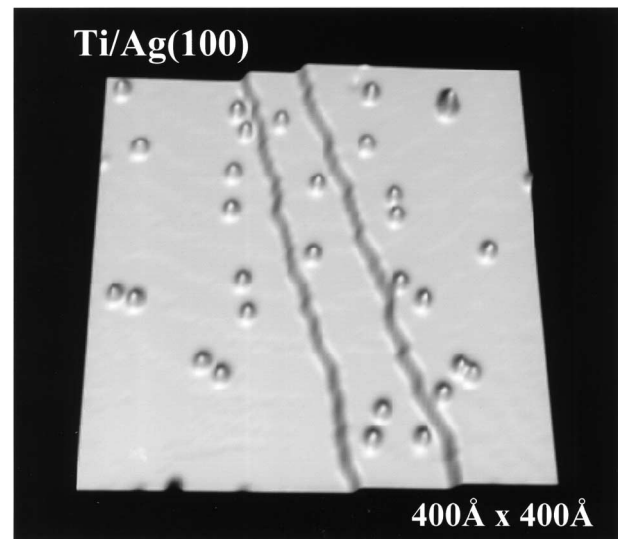

FIG. 1. Constant-current topograph showing the Ag(100) surface after deposition of $\sim$0.002 monolayer of Ti (400 Å × 400 Å, $I = 0.5 \times 10^{-9}$ A, $V = 0.10$ V, $T = 6.8$ K).

The dI/dV spectrum of an individual Ti atom at $T = 6.8$ K can be seen in Fig. 2. The dominant feature of this spectrum is the sharp edge that rises as voltage is increased over a width of 10 mV at $V = 0$ (this corresponds to the Fermi level, E_F). Similar spectra were reproduced for dozens of differently prepared STM tips on dozens of different Ti monomers [spectra taken over bare Ag(100) revealed no features in this energy range]. This spectrum is similar to Ti monomer spectra measured on Au(111) [12]. As with the Ti/Au(111) system, the spectrum shown in Fig. 2 can also be decomposed into a narrow Fano resonance at E_F and a broader Fano resonance located slightly above E_F. The dashed lines of Fig. 2 show these two components and the good fit that is obtained from their sum [13]. Each of these two Fano resonance components has the following function form [4,5,7,8,14–16]:

$$\frac{dI}{dV}(V) \propto \frac{(\varepsilon' + q)^2}{1 + \varepsilon'^2}, \qquad \varepsilon' = \frac{eV - \varepsilon_0}{\Gamma}. \quad (1)$$

Here q reflects the quality of the tip-adsorbate coupling, ε_0 is the energy location of the resonance, and 2Γ is the resonance width (FWHM) [4,5,7,8,14–16]. The narrow resonance seen at E_F in Fig. 2 has a width of only 10.5 mV, and so is identified as a Kondo resonance [8,12]. The other, broader, resonance has a width of 78 mV, and thus likely originates from a bare Ti d resonance [12].

In order to achieve the goal of observing the temperature dependence of the Kondo resonance, dI/dV spectra

were measured on individual Ti atoms over the temperature range $T = 6.8$–49.0 K. At each temperature the STM and sample were allowed to thermally equilibrate over 12 hours, and at least 15 spectra were acquired and averaged. Figure 3(a) shows the results of these measurements. The sharp edge of the Kondo resonance is seen to strongly broaden as the temperature is increased. We note that, while the observed spectral line shapes reveal intrinsic adatom electronic behavior, the relative *overall* amplitude between spectra does not reflect an intrinsic adatom property due to the use of different tips at different temperatures and the subsequent presence of constant multiplicative offsets in dI/dV. The curves are thus normalized at E_F.

It is nontrivial to extract intrinsic, temperature dependent density-of-states features from tunneling spectra because of the existence of thermal smearing introduced by the tunneling mechanism. The role of thermal smearing in tunneling measurements can be seen in a standard relation for STM dI/dV spectra [17]:

$$\frac{dI}{dV}(V, T) = \int_{-\infty}^{\infty} \rho_t \rho_s(E, T) \frac{d}{dV} F(E - eV, T) \, dE. \quad (2)$$

Here $\rho_S(E, T)$ is the desired energy and temperature dependent local density of states (LDOS) of the surface (a Ti monomer in our case), ρ_t is the LDOS of the STM tip (assumed to be featureless based on bare Ag spectra), and $F(E, T)$ is the Fermi-Dirac distribution function. In order to extract intrinsic Ti LDOS features from our spectra at higher temperatures, two Fano resonance line shapes (as shown in Fig. 2) were summed and thermally broadened using Eq. (2) before being fitted to each experimental spectra in Fig. 3(a) (the fit quality at each temperature was at least as good as that seen in Fig. 2). The results of this iterative thermal deconvolution procedure can be seen in Fig. 3(b), which shows the temperature dependent Kondo
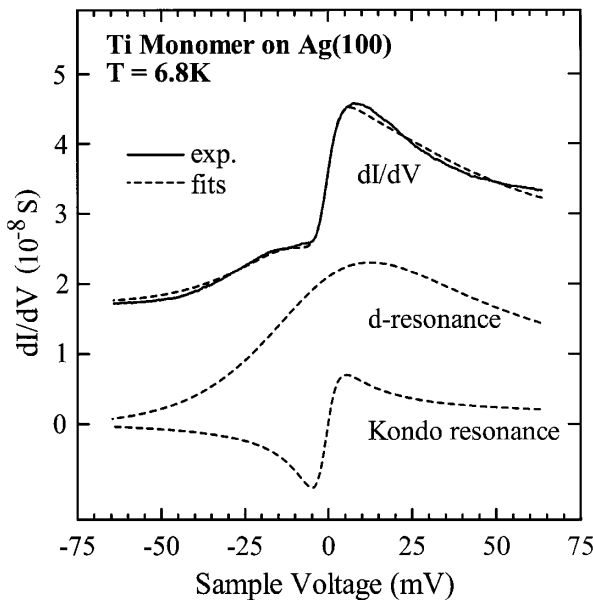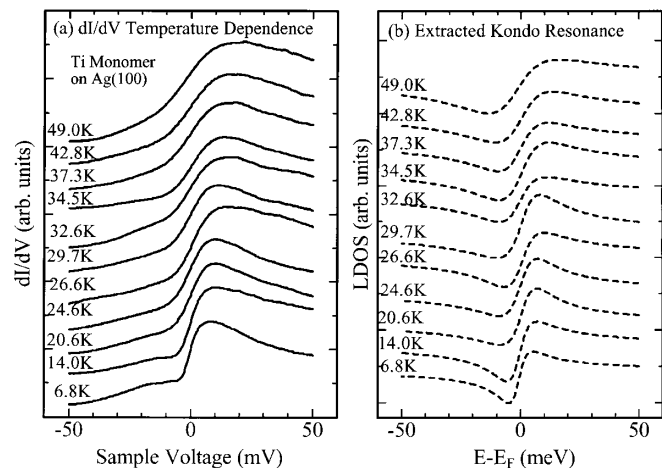
FIG. 2. The solid curve shows the dI/dV spectrum of a single Ti monomer on Ag(100) at 6.8 K. The dashed curves show two Fano resonances extracted from the experimental spectrum and the fit that is obtained by summing them [13]. The two extracted resonances are identified as a Kondo resonance and a Ti bare d resonance (the fit resonances have been shifted vertically for viewing).

FIG. 3. (a) Average dI/dV spectra of Ti monomers over the temperature range $T = 6.8$–49.0 K. (b) Intrinsic temperature dependence of the Ti Kondo resonance extracted from the spectra in (a) after the thermal deconvolution described in text.

component of the Ti LDOS. These curves are devoid of thermal smearing introduced via the tunneling mechanism and thus show the intrinsic temperature dependent broadening of the Ti Kondo resonance.

The extracted Kondo resonance spectral features shown in Fig. 3(b) allow us to quantitatively determine the temperature dependence of the Kondo resonance width for a single magnetic impurity. This width is represented by the "Γ" factor in Eq. (1), and was determined for the Kondo resonance at each temperature by using the fitting and thermal deconvolution procedure just described (uncertainty in this quantity was calculated by varying the characteristics of the two resonances used in the fitting procedureand finding the outlying parameters

$$\rho_d(E,T) = \frac{1}{\pi}\mathrm{Im}G_d(E,T) = \frac{1}{\pi}\frac{\mathrm{Im}\Sigma_d(E,T)}{\{E - [E_d + \mathrm{Re}\Sigma_d(E,T)]\}^2 + [\mathrm{Im}\Sigma_d(E,T)]^2}. \tag{3}$$

E_d represents the bare d-orbital energy and $\Sigma_d(E,T) = \mathrm{Re}\Sigma_d(E,T) + i\,\mathrm{Im}\Sigma_d(E,T)$ is the complex self-energy of the interacting impurity. In the low temperature, Fermi liquid regime, one can make the following approximation for the electronic self-energy of a Kondo impurity [3]:

$$\mathrm{Re}\Sigma_d(E,T) \approx -E_d, \tag{4}$$

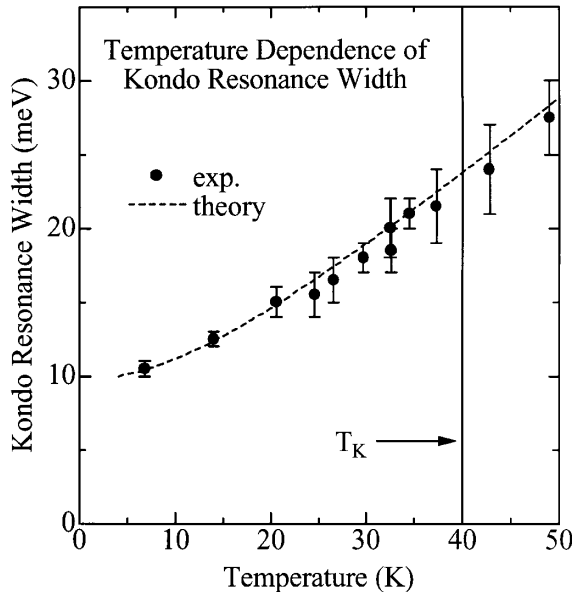$$\mathrm{Im}\Sigma_d(E,T) \approx \Delta + \gamma(E,T), \tag{5}$$

FIG. 4. Temperature dependence of the Kondo resonance width. The circles show the experimental widths obtained from the extracted Kondo resonance components shown in Fig. 3. The dashed curve shows the theoretical temperature dependence [Eq. (8)] for a Kondo impurity in the Fermi liquid regime with $T_K = 40$ K.

where the fit significantly worsened). Figure 4 shows a plot of the resulting intrinsic Kondo resonance width from $T = 6.8$ K to $T = 49.0$ K. The width increases quadratically with temperature at low temperatures, but becomes linear in temperature as the temperature is raised above 20 K.

The observed temperature dependence of the Kondo resonance can be understood within the context of the Anderson impurity model [3,18]. Here the Kondo resonance arises from the LDOS of an impurity d orbital that has a high charging energy and is coupled to an electron bath. The impurity LDOS $[\rho_d(E,T)]$ can be obtained from the imaginary part of the d-orbital Green function, $G_d(E,T)$ [3]:

$$\gamma(E,T) = \frac{1}{2}\Delta\left[\left(\frac{E}{k_B T_K}\right)^2 + \pi^2\left(\frac{T}{T_K}\right)^2\right]. \tag{6}$$

Δ represents the energy width of the bare d orbital (typically on the order of 100 meV [2]) and T_K is the impurity Kondo temperature. The imaginary part of the self-energy is especially relevant for this work, as it reflects the relaxation processes that determine the width of the Kondo resonance. The two terms in Eq. (5) show that there are two dominant processes at work here. The first term, Δ, corresponds to tunneling from the d orbital to surrounding conduction states, while the second term, $\gamma(E,T)$, corresponds to electron-electron scattering. $\gamma(E,T)$ reflects the fact that, as energy and temperature are increased, an electron in the Kondo "screening cloud" is more likely to be inelastically scattered by a conduction electron. This scattering rate scales with $1/T_K^2$.

In the Kondo regime $\Delta/k_B T_K \gg 1$, and so we can clarify the expected behavior of a Kondo impurity by making the following approximation:

$$\rho_d(E,T) \approx \frac{1}{\pi}\frac{1}{\mathrm{Im}\Sigma_d(E)}$$

$$= \frac{1}{\Delta\pi}\left[1 + \left(\frac{\pi T}{\sqrt{2}\,T_K}\right)^2\right]^{-1}$$

$$\times \frac{1}{1 + \left(\frac{E}{\sqrt{(\pi k_B T)^2 + 2(k_B T_K)^2}}\right)^2}. \tag{7}$$

The Kondo resonance is thus seen to be approximated by a Lorentzian resonance having an energy width (FWHM) as follows:

$$\mathrm{width} = 2\sqrt{(\pi k_B T)^2 + 2(k_B T_K)^2}. \tag{8}$$

The dashed line in Fig. 4 shows a fit of Eq. (8) to our measurements of the temperature dependence of the Kondo

resonance width. The only fitting parameter here is T_K, and a good fit is obtained for $T_K = 40$ K. The observed temperature dependence is thus well explained by electron-electron scattering in the Kondo regime [i.e., it arises from the $\gamma(E,T)$ term in Eq. (5)]. The T_K value extracted here for Ti/Ag(100) is consistent with T_K values observed for other surface Kondo systems [8,12,19], and is considerably less than T_K values observed for Ti impurities in the bulk [2]. The latter is expected, since bulk impurities are more highly coordinated than surface impurities.

We note that the Fermi liquid approach of Eqs. (3)–(8) is valid only for $T < T_K$ [20]. For a more correct treatment in the regime $T \geq T_K$, one must include logarithmic behavior at high temperature and resort to numerical renormalization group methods [3]. Although the fit in Fig. 4 extends up through T_K, the simple analytical treatment presented here explains the basic phenomenology observed in the data and illuminates the role of electron-electron scattering in determining the temperature dependent behavior of Kondo impurities.

In conclusion, we have measured the intrinsic temperature dependence of the electronic structure of individual Ti Kondo impurities from $T \approx (1/6)T_K$ up through $T = T_K$. Our main finding is that the Kondo resonance broadens rapidly with temperature in a manner that is well explained by the predicted Fermi liquid behavior of a Kondo impurity. Electron-electron scattering inherent in the Kondo effect thus dominates the temperature dependence of Ti surface magnetic impurities.

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