

## Conductance and Kondo Effect in a Controlled Single-Atom Contact

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The tip of a low-temperature scanning tunneling microscope is brought into contact with individual cobalt atoms adsorbed on Cu(100). A smooth transition from the tunneling regime to contact occurs at a conductance of  $G \approx G_0$ . Spectroscopy in the contact regime, i.e., at currents in a  $\mu\text{A}$  range, was achieved and indicated a significant change of the Kondo temperature  $T_K$ . Calculations indicate that the proximity of the tip shifts the cobalt  $d$  band and thus affects  $T_K$ .

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The concepts of electronic transport in nanometer-sized structures differ from those describing macroscopic conductors [1]. Measurements of the conductance of metallic nanowires have been performed using break junctions, where a thin metal wire is mechanically ruptured, or with the scanning tunneling microscope. The results show that chemical properties become important in the extreme case of conduction through single atoms or molecules. In a single-atom contact the valence orbitals of the bridging atom act as conductance channels [2], each contributing a fraction of a conductance quantum  $G_0 = 2e^2/h$  (where  $e$  is the electron charge and  $h$  is Planck's constant) to the total conductance  $G$  according to the Landauer theory [3,4]. The transmission of each conductance channel is determined by the chemical environment.

In break junction experiments usually pure elemental metals are used to prepare the contact and the central atom is most likely the same element as the leads. The geometry of the junction and the chemical nature of the bridging atom are not directly controlled. Scanning tunneling microscopy (STM) adds more control to the experiment since the bridging atom can be a different element than the sample material or even a molecule with known orientation [5]. This opportunity is particularly appealing for magnetic atoms which exhibit the Kondo effect on nonmagnetic substrates. For temperatures below a characteristic Kondo temperature ( $T_K$ ) interaction of the localized spin of this atom with the surrounding conduction electrons leads to a many-body ground state in which the spin of the magnetic atom is screened [6]. This phenomenon, first discovered from anomalous transport properties [7], causes a sharp resonance close to the Fermi level in tunneling spectra with a peculiar Fano line shape [8,9]. By varying the distance of the tunneling tip from the adsorbed atom (adatom) the many-body Kondo ground state may be controllably modified.

Here we report on low-temperature STM experiments on individual Co adatoms on Cu(100) surfaces. When contacting a single atom with the tunneling tip, a smooth and reproducible transition from the tunneling regime to con-

tact occurs with a conductance of  $G = I/V \approx G_0$  (where  $I$  is the current and  $V$  is the sample voltage). The Cu(100) surface was chosen to provide stable adsorption sites for the Co adatoms. Furthermore, spectroscopy in the contact regime, i.e., at currents in a  $\mu\text{A}$  range, is performed without structural changes. The line shape of the resonance induced by the Kondo effect is significantly changed at contact and is analyzed in terms of a modified Kondo temperature. On the basis of model calculations we propose that, at contact, the Co  $d$  band shifts and thus affects  $T_K$ .

The experiments were performed with a homemade STM operated at 8 K and at a base pressure of  $10^{-9}$  Pa. The sample surface was cleaned by argon ion bombardment and annealing. Cobalt atoms were deposited onto the Cu(100) surface at 8 K using an electron beam evaporator and an evaporant of 99.99% purity. Electrochemically etched tungsten tips were prepared *in situ* by controlled indentation into the substrate until the spectroscopic signature of the Kondo resonance appeared as a sharp and reproducible feature in  $dI/dV$  spectra. Current-versus-displacement curves were acquired by approaching the tip toward the adatom at  $45 \text{ \AA s}^{-1}$  and simultaneously recording the current. Contact between the tip and the adatom was controllably performed and led to a reproducible contact conductance. Subsequent spectroscopy in contact was therefore performed by opening the feedback loop at the contact conductances of interest.

Figure 1(a) shows a typical conductance curve as acquired on an individual Co atom on Cu(100). As detailed in Ref. [10] the exponential part of the conductance curve reflects the tunneling regime where  $G \propto \exp(-1.025\sqrt{\Phi}\Delta z)$ , with  $\Phi$  the apparent barrier height and  $\Delta z$  the tip displacement. For this regime denoted by I in the inset of Fig. 1(a) we find  $\Phi \approx 3.5 \text{ eV}$ . At  $\Delta z \approx -3.7 \text{ \AA}$  the slope increases and a continuous transition [11] (region II) occurs from the tunneling to the contact regime (region III). The latter is reached at  $\Delta z \approx -4.1 \text{ \AA}$  with a contact conductance of  $G \approx G_0$  and is characterized by a small slope (which would correspond to  $\Phi \approx 0.3 \text{ eV}$ ). No indication of con-

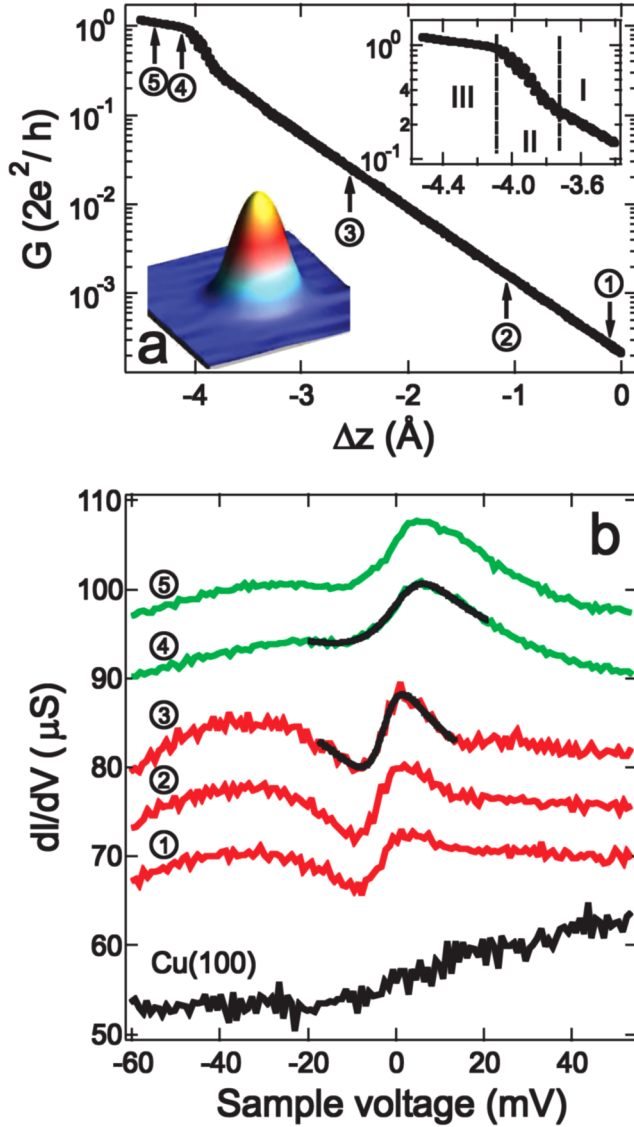


FIG. 1 (color online). (a) Conductance  $G$  versus tip displacement  $\Delta z$ . Top inset: Transition (II) from tunneling (I) to contact (III) regime. Bottom inset: Pseudo-three-dimensional representation of an STM image of a single Co atom. Conductance measurements were performed with the tip placed above the maximum height. (b) Spectra of  $dI/dV$  acquired at conductances indicated in (a). Lowest curve: Spectrum of Cu(100) at  $5 \mu\text{A}$ . Curves 1, 2, 3: Spectra of single Co atom in the tunneling regime at 1, 10, and 100 nA. Curves 4, 5: Spectra of single Co atom in the contact regime at 5.5 and  $6 \mu\text{A}$ . Solid lines show calculated Fano profiles with  $q = 1.2$ ,  $T_K = 78 \text{ K}$  (spectrum 3) and  $q = 2.1$ ,  $T_K = 137 \text{ K}$  (spectrum 4).

ductance quantization to an odd multiple of  $G_0/2$  was observed.

In Fig. 1(b) we present spectra of  $dI/dV$  in the tunneling (1,2,3) and contact (4,5) regimes. The lowest spectrum shows the  $dI/dV$  signal recorded with the same tip in close proximity to clean Cu(100). We find the spectroscopic signature of the Kondo effect around zero sample voltage

[8,9,12,13]. Intriguingly, this resonance is likewise observed in the contact regime. By imaging the surface area prior to and after the contact spectroscopy we verified that the tip and the sample surface remained unchanged and that the adsorption site of the Co atom was not modified. Comparing with spectra from the tunneling regime the current noise is appreciably lower at contact. Consequently,  $dI/dV$  spectroscopy with the tip of a scanning tunneling microscope in contact with an individual atom is feasible in a controlled and reproducible way.

Comparison of spectra 1–3 and 4,5 reveals a modified line shape at contact. Most notably, the line appears broadened compared to the tunneling regime. To analyze the resonance broadening it is useful to describe the spectroscopic signatures by a Fano line shape:

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

with  $\epsilon = (eV - \epsilon_K)/k_B T_K$  (where  $\epsilon_K$  is the resonance position and  $k_B$  is Boltzmann's constant) and  $q$  the asymmetry parameter of the Fano theory [14]. Using Eq. (1) it is indeed possible to fit the data in Fig. 1(b). The additional width of the resonance at contact is reflected by an increased Kondo temperature as expected [15].

In Fig. 2 we compare experimentally determined (circles) and calculated (triangles) Kondo temperatures. An abrupt change of  $T_K$  at a displacement of  $\approx -4.1 \text{ \AA}$  is observed in both data sets. For displacements  $> -4.1 \text{ \AA}$  experimental and theoretical Kondo temperatures vary between 70 and 100 K. In the contact regime ( $\Delta z < -4.1 \text{ \AA}$ ) experimental Kondo temperatures vary between 140 and 160 K while theoretical values scatter within 200–290 K. The abrupt broadening of  $dI/dV$  spectra upon contact [see the upper two spectra in Fig. 1(b)] can thus be related to a sudden increase of  $T_K$  as depicted in Fig. 2.

To determine the origin of the shift in the Kondo temperature we simulated the electronic structure of a coupled surface-adatom-tip system with standard density func-

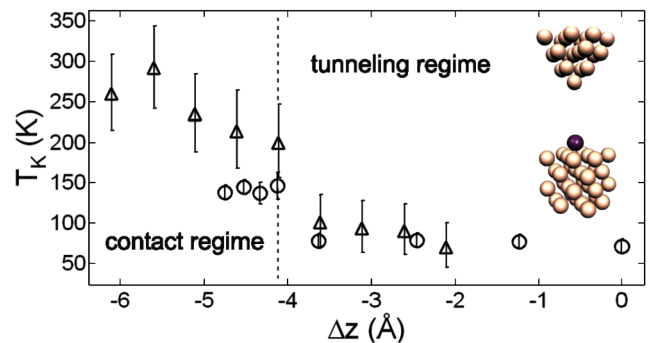


FIG. 2 (color online). Kondo temperature  $T_K$  versus tip displacement. Experimental data are depicted by circles; theoretical data are presented by triangles. The dashed line separates tunneling and contact regimes. Inset: Geometry of surface-adatom-tip setup for calculations.

tional theory (DFT) [16]. The setup of the system at a distance of 7 Å between adatom and tip is shown in the inset of Fig. 2. However, the Kondo effect is a genuine many-body phenomenon, and therefore the results of ground state DFT simulations cannot be directly related to the Kondo temperature. Here, we used an approximation going back to the concept of an Anderson impurity; in this case  $T_K$  is described by [6,12,22]

$$T_K \approx \frac{1}{k_B} \sqrt{\frac{\Delta U}{\pi}} \exp \left[ -\frac{\pi}{\Delta} \left( \left| \frac{1}{\epsilon_d} \right| + \left| \frac{1}{\epsilon_d + U} \right| \right)^{-1} \right]. \quad (2)$$

Within the single-orbital Anderson model,  $\Delta$  is the width of the impurity state. In the case of several impurity levels, as for the Co adatom, it denotes the broadening due to the crystal field splitting between these levels. The parameter  $\epsilon_d$  is the energy difference between the occupied  $d$ -band center and the Fermi level, and  $U$  the on-site Coulomb interaction between spin-up and spin-down states. All of these variables are readily accessible from ground state DFT simulations, if one assumes that the crystal field splitting, which describes the interaction between magnetic states of the impurity and the conducting electrons of the metal substrate, is correctly described by DFT [12]. The crystal field splitting shows up as the half-width of the spin-up density of states (DOS) of the  $d$  band. The problem then is transformed into finding the center of the occupied (spin-up)  $d$  band of the impurity, its half-width  $\Delta$ , and the exchange splitting  $U$ . It also follows from this simplified model that the main contributions to a change of the Kondo temperature will be a shift of the  $d$  band and a broadening or narrowing of the band. In addition, one expects qualita-

tively that  $\Delta$  will increase with an increased coordination number of a magnetic impurity.

In Fig. 3 we show the spin-polarized density of  $d$  states at the position of the Co impurity. It can clearly be seen that the main changes during an approach occur in the spin-up band of the magnetic impurity. Generally speaking, the result of closer proximity of the tip is a shift of the band toward the Fermi level and a broadening of the individual peaks, which is in agreement with [23]. The result is understandable, considering that the  $d$ -level width is a measure of the hybridization with the conduction electrons in the Cu sample and the tip. Lowering the tip increases the hybridization with the tip electrons.  $\Delta$  in this case is increasing as well as the effective exchange coupling and consequently the Kondo temperature. We calculated the on-site Coulomb interaction  $U$  between spin-up and spin-down states by estimating the center of the  $d$  band for occupied and unoccupied states. The center of the spin-up band is shown in the inset of Fig. 3. The value we obtain for the tunneling regime at a tip displacement of  $-2.1$  Å is  $U = 2.4$  eV, which is slightly lower than the value for Co on Au(111) [24]. This value decreases until it reaches  $U = 1.9$  eV in the contact regime. In addition, the three distinct peaks in the partial DOS merge to a single peak at the contact point. This leads to an increase in the crystal field splitting from 0.24 eV in the tunneling regime to 0.40 eV at contact. The crystal field splitting was obtained by fitting the peaks in the DOS to a Gaussian. The method is not very precise and the subsequent evaluations of  $T_K$ , using Eq. (2), reflect the error bar of about  $\pm 0.02$  eV in this evaluation. The difference between our estimate of  $\Delta = 0.24$  eV in the tunneling regime and previous work obtaining  $\Delta = 0.20$  eV [12] may partly be due to this evaluation method. However, also in this case the qualitative trend should be that the Kondo temperature increases during the tip approach. In Fig. 2 calculated Kondo temperatures as a function of the tip displacement are depicted as triangles. We observe a close to constant Kondo temperature for  $\Delta z > -4.1$  Å of about 70–100 K, in agreement with experimental values. The Kondo temperature increases in a steplike fashion if the tip displacement decreases below this value. In the contact regime,  $\Delta z < -4.1$  Å, we find a Kondo temperature of about 200–290 K, in good agreement with the expected value of 300 K for a magnetic impurity in the bulk. Because of the increased crystal field splitting with decreasing displacement, i.e., decreasing tip-adatom separation, and decreasing exchange splitting between spin-up and spin-down band,  $T_K$  increases during the approach until it reaches the bulk value of about 300 K [25]. However, the simulated values in this case are about 40%–50% above the values obtained in the experiments. While we cannot completely rule out that our simple model in this case does not do justice to the physical situation, we assume that the deviation is rather due to limitations of the simulated system. The surface-adatom-tip system in the

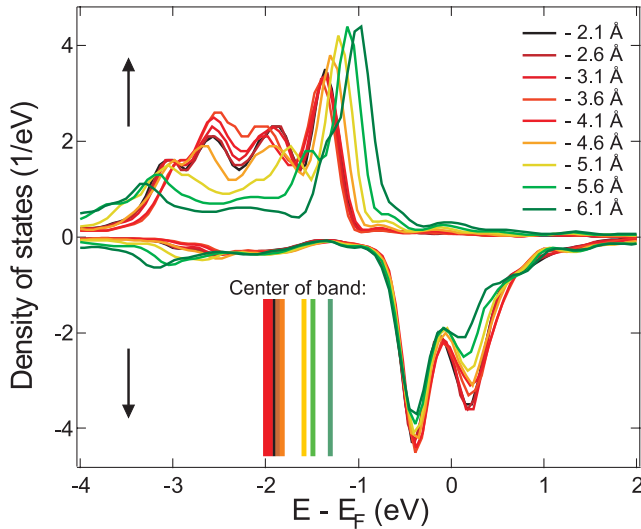


FIG. 3 (color online). Density of  $d$  states (DOS) versus tip displacement. Spin-up ( $\uparrow$ ) and spin-down ( $\downarrow$ ) DOS is plotted as positive and negative values, respectively. The  $d \uparrow$  band is shifted toward the Fermi energy with decreasing displacement. Inset: Center of the  $d$  band calculated statistically over occupied spin-up states.

simulations is very rigid due to the limited number of crystal layers on either side. In addition, the tip in the experiments is a metal alloy comprising an interface between tungsten and most likely Cu atoms from the surface, while it is a single Cu crystal in the simulations. These deviations between the experimental and the simulated physical systems may account for the slight deviations in the contact regime. However, it has to be stressed that both the absolute values for  $T_K$  as well as the significant change occurring at the displacement of  $\approx -4.1 \text{ \AA}$  are very well accounted for in the simulations. Moreover, it is clear that the shift of the  $d$  band due to the field of the tunneling tip and the reduction of the exchange splitting in this process are the main causes for the observed variations.

In conclusion,  $dI/dV$  spectroscopy of individual metal adatoms in contact with the tip of a scanning tunneling microscope is feasible. These experiments will complement measurements using mechanical break junctions and offer additional possibilities. The sample area for spectroscopy can be imaged prior to and after contact measurements, and there is more control over the atom or molecule bridging the electrodes. For Co atoms on Cu(100) we observe a modified line shape near the Fermi energy which can be described by an increased Kondo temperature. Model calculations indicate a shift of the Co  $d$  band at contact and a concomitant change of  $T_K$ .

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