Conductance and Kondo effect of a controlled single atom contact

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The tip of a low-temperature scanning tunneling microscope is brought into contact with individual Kondo impurities (cobalt atoms) adsorbed on a Cu(100) surface. A smooth transition from the tunneling regime to a point contact with a conductance of $G \approx G_0$ occurs. Spectroscopy in the contact regime, i. e., at currents in a µA range was achieved. A modified line shape is observed indicating a significant change of the Kondo temperature $T_K$ at contact. Model 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 drastically 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 $G_0 = 2e^2/h$ (e: electron charge, h: Planck’s constant) to the total conductance $G$ according to the Landauer formula $G = G_0 \sum_i T_i$. The transmission $T_i$ of the $i$-th channel is determined by the chemical environment. When $T_i$ is spin dependent, the sum extends over both spin channels with a maximum conductance of $G_0/2$ per channel. Complete spin polarization and perfect transmission of the relevant channels may lead to conductance quantization to integer multiples of $G_0/2$. While this case is not expected from calculations [3, 4, 5, 6], there are contradictory experimental reports [7, 8, 9, 10, 11, 12].

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 element 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 [13]. This opportunity is particularly appealing for magnetic atoms which exhibit the Kondo effect on nonmagnetic substrates. By varying the distance of the – either magnetic or nonmagnetic – tunneling tip from the adsorbed atom (adatom) the many-body Kondo ground state may be controllably disturbed.

Here we report on low-temperature STM experiments on individual Co adatoms on Cu(100) surfaces which in spectra of the differential conductance $(dI/dV)$ exhibit a Fano line shape owing to the Kondo effect. When contacting a single atom with the tunneling tip a smooth and reproducible transition from the tunneling regime to contact occurs with a conductance of $G = I/V \approx G_0$ ($I$: current, $V$: 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 µA range is performed without structural changes. The line shape is significantly changed at contact and is analysed in terms of a modified Kondo temperature $T_K$. 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 home-made scanning tunneling microscope 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. The tip was 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˚A s$^{-1}$ and simultaneously recording the current. Contact formation 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 1a shows a typical conductance curve as acquired on an individual Co atom on Cu(100). As detailed in Ref. [14] the linear 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. 1a, we find $\Phi \approx 3.5$ eV. At $\Delta z \approx -3.7$ Å the slope increases and a continuous transition [15] (region II) occurs from tunneling to contact regime (region III). The latter is reached at $\Delta z \approx -4.1$ Å and is characterized by a small...
FIG. 1: (Color online) (a) Conductance $G$ versus tip displacement $\Delta z$. Inset: Transition (II) from tunneling (I) to contact (III) regime. (b) Spectra of $dI/dV$ acquired at positions indicated in (a). Lowest curve: Spectrum of Cu(100) at 5 µA. Curves 1, 2, 3: Spectra of single Co atom in the tunneling regime at 1 nA, 10 nA, 100 nA. Curves 4, 5: Spectra of single Co atom in the contact regime at 5.5 µA, 6 µA. Solid lines show calculated Fano profiles with $q = 1.2$, $T_K = 78$ K (spectrum 3) and $q = 2.1$, 137 K (spectrum 4).

slope (which would correspond to $\Phi \approx 0.3$ eV). In agreement with the conclusions of Ref. 12 for break junctions of magnetic metals we find that a single atom Co contact in a scanning tunneling microscope does not exhibit a conductance of $G_0/2$.

In Fig. 1(b), we present spectra of $dI/dV$ in the tunneling (spectra 1,2,3) and contact (spectra 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 resonance around zero sample voltage $\epsilon_K$ of Co on Cu(100) [19]. 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 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 analyse broadening of the resonances it is useful to describe the spectroscopic signatures by a Fano line shape

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

with $\epsilon = (eV - \epsilon_K)/k_BT_K$ ($\epsilon_K$: position of Kondo resonance, $k_B$: Boltzmann’s constant) and $q$ the asymmetry parameter of the Fano theory [20]. Using Eq. (1) it is indeed possible to fit the data in Fig. 1b. The additional width of the Fano feature at contact is reflected by an increased Kondo temperature as expected [21].

In Fig. 2 we compare experimentally determined (circles) and calculated (triangles) Kondo temperatures. An abrupt change of $T_K$ at a displacement of $\Delta z \approx -4.1$ Å is observed in both data sets. For displacements $\Delta z > -4.1$ Å experimental and theoretical Kondo temperatures vary between 70 – 100 K. In the contact regime, i.e., $\Delta z < -4.1$ Å, 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 formation (see the upper two spectra in Fig. 1b) can thus be related to a sudden increase of the Kondo temperature 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 functional theory (DFT) [22]. However, a Kondo resonance is a genuine many-body effect, the results of
groundstate DFT simulations can therefore not directly be related to the Kondo temperature. Here, we used an approximation going back to the concept of an Anderson impurity; in this case the Kondo temperature $T_K$ is described by [15, 28, 29].

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

where $\Delta$ is the crystal field splitting, $\epsilon_d$ the energy difference between the occupied $d$-band center and the Fermi level, and $U$ the exchange splitting between spin-up and spin-down states. All of these variables are readily accessible from groundstate DFT simulations, if one assumes that the crystal field splitting $\Delta$, which describes the interaction between magnetic states of the impurity and the conducting electrons of the metal substrate, is correctly described by DFT simulations [15], where it shows up as the halfwidth 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 halfwidth $\Delta$, 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. A similar conclusion was drawn to explain the disappearance of the Kondo resonance for Co dimers on Au(111) [30]. In addition, one expects qualitatively 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. Both of these features indicate, qualitatively, that the Kondo temperature should increase. We calculated the exchange splitting $U$ 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 $\Delta z = -2.1 \, \text{Å}$ is $U = 2.4 \, \text{eV}$, which is slightly lower than the value for Co on Au(111) [31]. This value decreases until it reaches $U = 1.9 \, \text{eV}$ 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 $0.24 \, \text{eV}$ in the tunneling regime to $0.40 \, \text{eV}$ 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 the Kondo temperature $T_K$, using Eq. (2), reflect the error bar of about $\pm 0.02 \, \text{eV}$ in this evaluation. The difference between our estimate of $\Delta = 0.24 \, \text{eV}$ in the tunneling regime and previous work obtaining $\Delta = 0.20 \, \text{eV}$ [15] 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 $\Delta z > -4.1 \, \text{Å}$ of about $70 - 100 \, \text{K}$, in agreement with experimental values. The Kondo temperature increases in a step-like fashion if the tip displacement decreases below this value. In the contact regime, $\Delta z < -4.1 \, \text{Å}$, we find a Kondo temperature of about $200 - 290 \, \text{K}$, in good agreement with the expected value of $300 \, \text{K}$ for a magnetic impurity in the bulk.

Due to 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, the Kondo temperature increases during the approach until it reaches the bulk value of about $300 \, \text{K}$ [32]. 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 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
the Kondo temperature as well as the significant change occurring at the displacement of $\Delta z \approx -4.1 \text{Å}$ 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 $T_K$. Model calculations indicate a shift of the Co $d$-band at contact and a concomitant change of $T_K$.

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[23] [13] and [14]. The surface cell was mimicked by a $2\times2$ unit cell. In this case the distance between the Co adatoms is larger than 7 Å, which precludes coupling of adjacent Co adatoms in our periodic setup. The coupled system consisted of six Cu layers in (100) orientation, the tip apex was modeled by a two-layer pyramid. During the approach all coordinates of three surface layers, the adatom, and the tip apex were fully relaxed in $z$ direction to residual forces of less than 0.01 eV Å$^{-3}$. Relaxations were performed for the magnetic system, the electronic groundstate was simulated using the Perdew-Burke-Ernzerhof [24] parametrisation of the exchange correlation functionals as well as an all-electron method, the Projector-Augmented-Wave method [25]. The convergence of the electronic structure of the coupled system with the number of $k$ points in the irreducible wedge was carefully checked; since the C$4v$ symmetry was retained during the approach of the tip, the number of $k$ points to achieve convergence could be reduced to $6 \times 6 \times 1$ $k$ points in a Monkhorst-Pack grid [26].
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