Kondo Effect in Single Atom Contacts: The Importance of the Atomic Geometry

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(Received 25 July 2008; published 18 November 2008)

Co single atom junctions on copper surfaces are studied by scanning tunneling microscopy and *ab initio* calculations. The Kondo temperature of single cobalt atoms on the Cu(111) surface has been measured at various tip-sample distances ranging from tunneling to the point contact regime. The experiments show a constant Kondo temperature for a whole range of tip-substrate distances consistently with the predicted energy position of the spin-polarized *d* levels of Co. This is in striking difference to experiments on Co/Cu(100) junctions, where a substantial increase of the Kondo temperature has been found. Our calculations reveal that the different behavior of the Co adatoms on the two Cu surfaces originates from the interplay between the structural relaxations and the electronic properties in the near-contact regime.

DOI: 10.1103/PhysRevLett.101.216802 PACS numbers: 73.63.Rt, 68.37.Ef, 71.15.Ap, 73.20.Hb

The electron transport properties in a circuit, whose dimensions are reduced to single atom or molecule contact, is dominated by the quantum character of matter [1] and requires a deep understanding of its nanometer scale properties. Additionally, the electron transport through such a junction is strongly influenced by the coupling of the orbitals of the electrodes to the bridging molecule or atom [2]. Accessing the correct information of the geometrical arrangement of the contact is fundamental to the interpretation of the experimental data. This is often challenging, despite the continuous progress in understanding the electron transport through nanometer scale junctions [3–10]. Among other techniques such as mechanical controlled break junction [3,4,6] or electromigration [11], a junction achieved with the tip of a scanning tunneling microscope (STM) on a metal surface [7–9,12] has been proven as a valuable tool to target and select the substrate configuration before and after the contact is formed. Nonetheless, a general picture on the influence of atomistic order on the electron conductance at nanometer scale junctions is, at present, still missing.

Co adatoms on copper surfaces constitute an ideal system for studying the electron transport through nanometer scale junctions. The interaction of the unpaired electrons of single Co atoms with the free electron states on copper surfaces leads to the formation of a narrow electronic resonance at the Fermi level known as the Kondo resonance. This has been extensively characterized in tunneling conditions [13–15]. One main result of these studies is the evidence that on different supporting surfaces the width of this resonance coincides with a change of the occupation of the *d* electron levels of the Co adatom [14]. This inherently reflects a varied coupling of the magnetic impurity to the metal substrate. Indeed, a simple model has been suggested to relate the energy position of the electron *d* levels of the impurity and the atomic arrangement in close proximity of the Co adatom [14,15]. Specifically, a narrower Kondo resonance is observed for Co adatoms on Cu(111) than on the Cu(100) surface in agreement with a shift in energy of the *d* levels, i.e., with an increase in their occupation from the first to the second surface [14,15]. Because of this dependence, the width of the Kondo resonance is then a good reference parameter to characterize the influence of the tip at reduced distances. However, it is *a priori* not evident if the width of the Kondo resonance will follow a trend similar to the one observed in tunneling configuration on various surfaces also when the tip is approached to the point contact configuration.

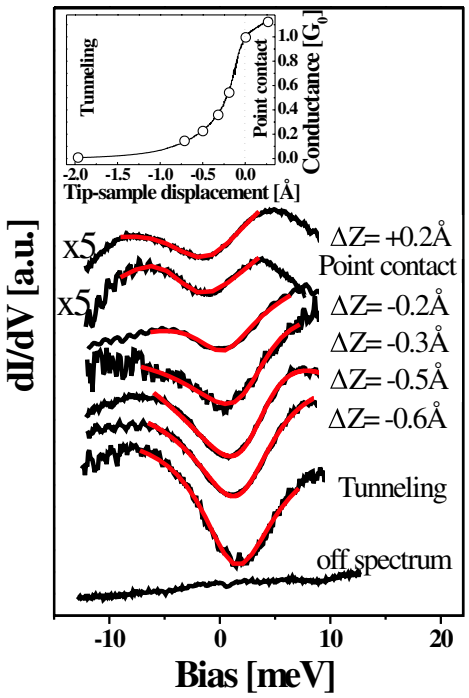
In order to address this question we measured the current-voltage characteristics at different tip-sample distances ranging from tunneling to point contact on individual Co adatoms on a Cu(111) surface. As will be shown in the following, the width of the Kondo resonance is practically constant on this surface at all tip-substrate distances in an apparent contradiction with the previously reported results on Cu(100) [8].

Based on *ab initio* theoretical calculations aimed to determine the electronic and magnetic properties of these two systems, we will show that the opposing results observed on the two copper surfaces are not contradicting but demonstrate nicely the determining influence of the local atomic structure on the transport properties of a nanoscale junction.

The experiments were performed using a home built scanning tunneling microscope operated at 6 K in ultra high vacuum (UHV) with a base pressure of 1×10^{-11} mbar.

The Cu(111) single crystal has been cleaned in UHV by cycles of Ar^+ ion sputtering and annealing. Co single atoms were deposited on the Cu surface at 20 K from a thoroughly degassed Co wire wound around a tungsten filament. This resulted in a coverage of about 10^{-3} ML of isolated immobile Co adatoms. The STM tip, electrochemically etched from tungsten wire, was treated *in vacuo* by electron field emission and soft indentation into the copper surface. This assured a spectroscopically featureless tip near the Fermi energy. Given this preparation, the tip was most likely covered by copper atoms deriving from the substrate.

The inset in Fig. 1 shows the conductance of a single Co adatom at various tip-substrate displacements. This has been achieved by recording the current while approaching the tip towards the atom, in open feedback loop conditions. As the tip-substrate distance is reduced the current increases smoothly from the tunneling to the point contact regime following the exponential dependence with the tip-substrate distance (z) characteristic of the electron tunneling process $I(z) = I_0 \exp(-Az)$ (where A is proportional to the work function of tip and substrate). Fitting the experimental curve, we obtained a work function for the Co/Cu(111) system of 5 eV. As the point contact regime is reached the current is found to exhibit a characteristic quantization plateau with only a weak dependence on the distance. The plateau is observed to be $1G_0$ where G_0 is the conductance quantum $G_0 = 2e^2/h$ (h is the Planck constant) in agreement with studies on Co/Cu(100) [8]. Topographic images acquired before and after the tip was approached and retracted from the point contact configuration confirm that the contact region as well as the tip have not changed during the tip displacements.



ΔZ [Å]	T_K[K]
0.2Å	51±4
Point contact	51±1
-0.2Å	49±2
-0.3Å	49±3
-0.5Å	49±2
-0.6Å	51±1
-2Å	51±2

FIG. 1 (color online). Conductance and dI/dV spectra for isolated Co atoms on a Cu(111) surface achieved at different tip-substrate distances ΔZ from tunneling to point contact. Prior to the point contact measurements the tip was stabilized at a defined sample distance, setting the tunneling conditions at 8 meV and 5 nA. In the inset a representative current vs tip displacement is shown. dI/dV spectra have been recorded at the positions indicated by circles in the inset. The curves are normalized to the tunneling current at the tip height location and a vertical offset has been added for a better visualization. The Kondo temperature T_K given on the right side of the image has been obtained fitting the curves with a Fano line shape (light line).

Information on the Kondo resonance has been obtained recording the dI/dV spectra on top of the Co adatom at various tip-substrate displacements. In Fig. 1, we report the spectra obtained at the tip-substrate separation indicated by the circles in the inset. The current versus voltage is measured with a lock-in amplifier applying a voltage modulation in the range of 1 to 0.1 mV (rms). All the curves obtained in the range from the initial tunneling ($\Delta Z = -2$ Å) to the point contact ($\Delta Z = 0.2$ Å) condition show a characteristic dip in the local density of states at an energy close to the Fermi level. This dip, which is due to the Kondo resonance, can be characterized according to its width ΔE, which is proportional to the Kondo temperature T_K, $\Delta E = 2k_B T_K$, where k_B is the Boltzmann constant [13,14]. The Kondo temperature can be extracted from these curves by fitting the experimental spectra with a Fano line function according to $dI/dV \propto (q + \epsilon)^2/(1 + \epsilon^2)$, with $\epsilon = (eV - \epsilon_K)/k_B T_K$ where q and ϵ_K define the asymmetry of the curve and the energy position of the resonance with respect to the Fermi energy [16]. The obtained Kondo temperature T_K is reported in Fig. 1 for each sampled tip position. As can be seen, the Kondo temperature for the Co on Cu(111) system is constant, within the experimental error, from the tunneling to the point contact regime. These results have been reproduced with different tips and different tip treatments which assured a spectroscopic featureless tip in the energy range of the Fermi level. Further details are given in Ref. [17].

The observed behavior of the Kondo temperature on the Cu(111) surface contrasts with the behavior previously reported for the Co/Cu(100) system, where a considerable increase of the Kondo temperature (from 70–90 K in tunneling to 150 K in point contact) was observed [8]. As will be shown below this difference can be ascribed to the sensitivity of the Kondo effect to the local atomic geometry.

To obtain a physical understanding of the structural sensitivity, we have modeled at first the atomic relaxation in the single Co atom junction under the influence of the tip proximity and then considered its consequence on the electronic structure. Indeed, reducing the tip-substrate separation can induce a local perturbation in the atomic ordering at the junction which can affect the coupling between the orbitals of the electrodes and of the Co atom

and consequently the electronic and the magnetic properties of the system. To simulate the nanoscale-junction on the atomic scale, we have performed molecule static (MS) calculations with many-body interatomic potentials fitted to the spin-polarized *ab initio* calculations [18]. In these simulations the tip has been represented as a pyramid consisting of 10 Cu atoms arranged in fcc(111) stacking. Figure 2 shows the variation of the tip-adatom and the adatom-substrate separations during the tip displacement [panels 2(a) and 2(b), respectively]. On a first glance one can see that beside an initial region, the tip-Co adatom as well as the Co adatom-substrate distances are not linearly proportional to the tip displacement. As the tip-substrate distance is reduced, the atomic order at the junction relaxes: the atoms of the tip, the Co impurity as well as the atoms of the substrate move to new equilibrium positions. The real tip-substrate distance is then a dynamic variable according to the specific location of the tip and to its attractive and repulsive interaction with the surface and the impurity. Specifically, up to the minimum distance of 5.3 Å, the tip-Co adatom distance is almost linear with the tip displacement. Approaching further, the distance between the opposite sides of the nanometer scale junction is reduced to a larger extent than the effectively applied tip displacement due to an attractive interaction (up to 4.7 Å). By reducing the tip-substrate distance below 4.7 Å, the interaction becomes repulsive. At this tip proximity, the adatom-substrate distance, defined as the vertical distance between the Co adatom and its first nearest neighbor, is strongly reduced while the distance between the tip and adatom is only slightly decreased. This implies that the Co adatom shifts towards the substrate. As a consequence when the point contact configuration is reached, the Co-Cu(111) surface distance compares to the equilibrium distance predicted for the tunneling condition [dotted line in panel 2(b)].

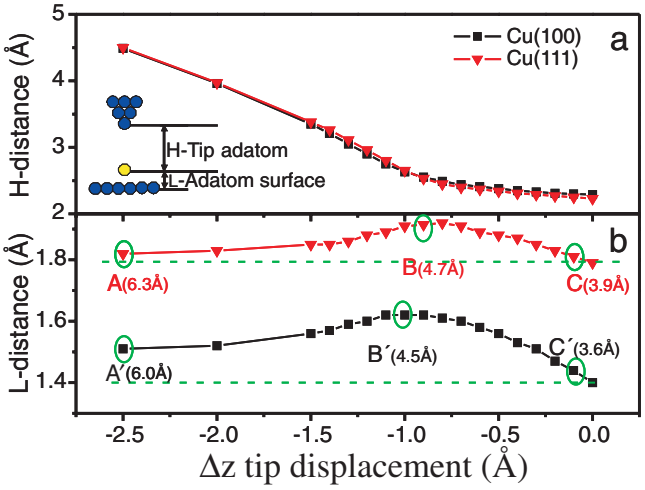


FIG. 2 (color online). Atomic relaxation at the single Co atom junction as a function of the tip displacement. The initial tip-adatom distance (H) is the same for Cu(111) and Cu(100) surfaces. The adatom-substrate (L) distances for Co adatom on the two surfaces is shown in panel (b). The dashed lines show the Co-substrate distance in point contact conditions. (A), (B), and (C) indicate the position where the LDOS shown in Fig. 3 have been calculated; the values in the brackets are the tip-substrate distances for these three positions [23].

Figure 2 compares also the atomic relaxation process on the two copper surfaces. The general trend of attractive and repulsive interaction of tip-atom and surface can be observed in both cases. However, differences in the atom dynamics under the influence of the tip and in the Co-surface distance are obvious. Specifically, under the influence of the tip the Co impurity is pushed deeper into the Cu (100) surface in point contact configuration [dotted line in panel 2(b)] than it is in tunneling conditions. Therefore, it can be expected that the stronger interaction with the surface increases on the Cu(100) substrate the hybridization of the d levels of the Co adatom with the sp states of the surface.

This and its consequence on the magnetic properties of the junction at various tip proximity can be understood by calculating the local density of states (LDOS) of the Co adatom. Spin-polarized calculations were performed within the linear combination of atomic orbital formalism by means of density functional theory implemented in SIESTA [19]. The geometry was optimized by SIESTA until all residual forces on each atom are smaller than 0.01 eV/Å [20,21].

In Fig. 3 the d levels of Co/Cu(111) are shown for different tip-substrate separations (denoted A, B, and C in Fig. 2) with the energies given with respect to the Fermi level. It can be seen that only the occupied density of states of the Co adatom on Cu(111) are slightly affected by the tip-substrate distance. Moreover, the energy differences between the center of the occupied spin-up band (or majority states) and the center of the partially unoccupied spin-down band (or minority states) U for three tip-substrate separations are close. Consistently, also the magnetic moment of the Co adatom at these three tip-substrate separations ($1.99\mu_B$, $1.96\mu_B$, and $1.78\mu_B$, respectively) are only slightly affected by the tip proximity. On the contrary a large energy shift of the d levels was reported for Co adsorbed on Cu(100) surface [8,22]. A comparison of the energy position of the occupied d levels is shown in Fig. 3(b). On both surfaces the position of the occupied d levels shifts towards higher energies under the influence of the tip proximity. On the Cu(111) surface this shift is, however, much smaller. On Cu(100) the substantial change in the occupation of the d levels is reflected in the increase of the Kondo temperature in point contact. The difference in the behavior of the Kondo temperature on Cu(111) and Cu(100) is caused by different atomic relaxations which occur on both substrates. For all tip positions the distance between the Co adatom and Cu(111) is significantly larger than that on Cu(100) (see Fig. 2). Therefore the hybridization of d states of Co adatoms with sp electrons of the substrate is weaker on Cu(111). As the result, only very

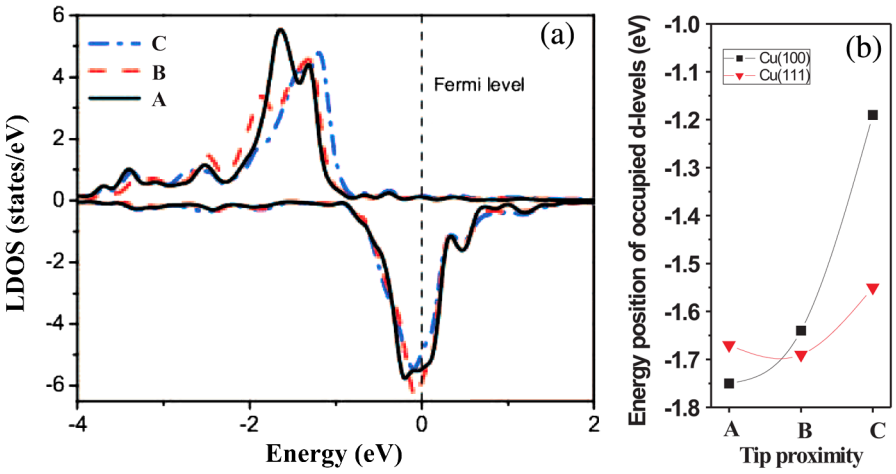


FIG. 3 (color online). Influence of the tip proximity on the d levels of Co atoms on Cu(111). (a) Spin-polarized LDOS for the d levels. The curves are calculated for tip-substrate displacements as denoted in Fig. 2. (b) Energy position of the occupied d-band center on Cu(111) and Cu(100) at different tip-substrate positions. The lines connecting the points are a guide to the eye.

small changes in the LDOS of Co adatoms are found on Cu(111). Accurate calculations of the Kondo temperature for our system are, however, not straightforward [8]. Nonetheless, the theoretical predictions and the experimentally observed Kondo temperature in the point contact regime follows the trend described by the model proposed by Wahl *et al.* [14] for the tunneling regime. The increase of the occupation of the d level effects sensibly the Kondo temperature on Cu(100) and almost negligibly on the Cu(111) surface.

In conclusion, the present experimental and theoretical work demonstrates that the local atomic geometry plays a major role in the electron transport properties of nanoscale junctions. The tip proximity in the point contact regime influences the atomic relaxation in the single atom junction and thereby determines the lattice equilibrium position. These structural relaxations induce a modification of the sp-d hybridization between the electrode surface and the bridging atom. While on the closed packed Cu surface the impurity d level is less affected, it shifts substantially on the open (100) surface. This explains the striking difference observed in the behavior of the Kondo temperature of Co adatoms upon point contact formation on Cu(111) and Cu(100). We believe that these results have general validity and might clarify a few of the uncertainties in the electron transport through nanometer scale junctions characterized by break-junction experiments.

We acknowledge P. Wahl for fruitful discussions. The work was supported by Deutsche Forschungsgemeinschaft (DFG SPP 1165, SPP 1243, and SSP 1153).

[1] G. Cuniberti, G. Fagas, and K. Richter, *Introducing Molecular Electronics*, Lecture Notes in Physics 680 (Springer Verlag, Berlin, 2005).
[2] Kun Tao *et al.*, Phys. Rev. B **78**, 014426 (2008).
[3] E. Scheer *et al.*, Nature (London) **394**, 154 (1998).
[4] A. Yanson *et al.*, Nature (London) **395**, 783 (1998).
[5] J. Pascual *et al.*, Science **267**, 1793 (1995).
[6] E. Lörtscher, H. B.Weber, and H. Riel, Phys. Rev. Lett. **98**, 176807 (2007).
[7] L. Bürgi, Ph.D. thesis, Lausanne, 1999.
[8] N. Néel *et al.*, Phys. Rev. Lett. **98**, 016801 (2007).
[9] R. Temirov, A. Lassise, F. Anders, and F. Tautz, Nanotechnology **19**, 065401 (2008).
[10] X. Xiao, B. Xu, and N. J. Tao, Nano Lett. **4**, 267 (2004).
[11] H. Park *et al.*, Nature (London) **417**, 722 (2002).
[12] J. Gimzewski and Möller, Phys. Rev. B **36**, 1284 (1987).
[13] V. Madhavan *et al.*, Science **280**, 567 (1998).
[14] P. Wahl *et al.*, Phys. Rev. Lett. **93**, 176603 (2004).
[15] N. Knorr *et al.*, Phys. Rev. Lett. **88**, 096804 (2002).
[16] U. Fano, Phys. Rev. **124**, 1866 (1961).
[17] See EPAPS Document No. E-PRLTAO-101-064846 for supplementary information. For more information on EPAPS, see http://www.aip.org/pubservs/epaps.html.
[18] N. Levanov *et al.*, Phys. Rev. B **61**, 2230 (2000).
[19] J. M. Soler *et al.*, J. Phys. Condens. Matter **14**, 2745 (2002).
[20] LDA approaches have been used for the exchange and correlation potential, and a 250 Ry energy cutoff is used to define real-space grid for numerical calculations involving the electron density. Core electrons of all elements are replaced by nonlocal norm-conserving Troullier-Martins pseudopotentials. Valence electrons of the Cu substrate are described using a double-ζ plus polarization atomic orbital basis set, and a triple-ζ plus polarization atomic orbital basis sets for the Co adatom.
[21] We chose three different tip-substrate distances (denoted A, B, and C in Fig. 2) and perform a full relaxation by SIESTA code. The displacements of the Co adatom at these positions calculated by the MS method are 0.02, 0.21, and 0.05 Å, respectively. These are 0.01, 0.26, and 0.08 Å obtained from SIESTA code, coinciding with the MS results very well. Relaxation of the atoms in the tip is also taken into account in our calculations [22].
[22] R. Huang *et al.*, Phys. Rev. B **73**, 153404 (2006).
[23] The initial position of the tip was chosen at the same distance from the Co adatom on both substrates. As the distance between the Co adatom and the substrate is larger on Cu(111) than that on Cu(100), the tip-substrate distance is also larger on the Cu(111) surface.

Electronic Physics Auxiliary Publication for "Kondo effect in single adatom contacts: the importance of the atomic geometry"

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Tip contributions to the Kondo resonance in point contact spectroscopy

During the point contact experiment on single Co atoms adsorbed on the Cu(111) surface, particular attention has been given to the spectroscopic configuration of the tip. It was electrochemically etched from a tungsten wire and treated *in vacuo* by electron field emission and soft tip indentations into the copper surface. This protocol was repeated till a spectroscopic featureless tip in the region of the Fermi level was obtained. In figure EPAPS 1a we show a second series of dI/dV spectra obtained on top of a Co adatom adsorbed on Cu(111) surface at different tip-substrate distances. The spectra reveal the characteristic Kondo resonance at the Fermi level whose width is constant at distances ranging from tunneling to the point contact regime. The observed Kondo temperature is 51K, in agreement with the spectra shown in figure 1. It is worth underlying that the reproducibility of these spectra has been assured by the tip preparation described before and showing a featureless spectrum on the copper substrate (off-spectrum).

In case these spectroscopic conditions of the tip are not satisfied, a broadening the Kondo resonance is observed. Representative spectra are shown in figure EPAPS 1b. While the Kondo temperature in tunneling conditions is only moderately broadened (61 K), in the point contact regime the Kondo resonance is sensibly affected. This leads to an apparent increase of the Kondo temperature to about 110K. As a general trend it is observed that the broadening of the Kondo resonance increases by reducing the tip-sample distance. However, the observed Kondo temperature is not reproducible and depends on the details of the tip spectroscopic conditions.

In conclusion, tip-features in the energy range of the Fermi level, which in tunneling conditions induce in most of the cases only a minor broadening of the Kondo resonance, dominate in the spectra achieved in point contact regime.

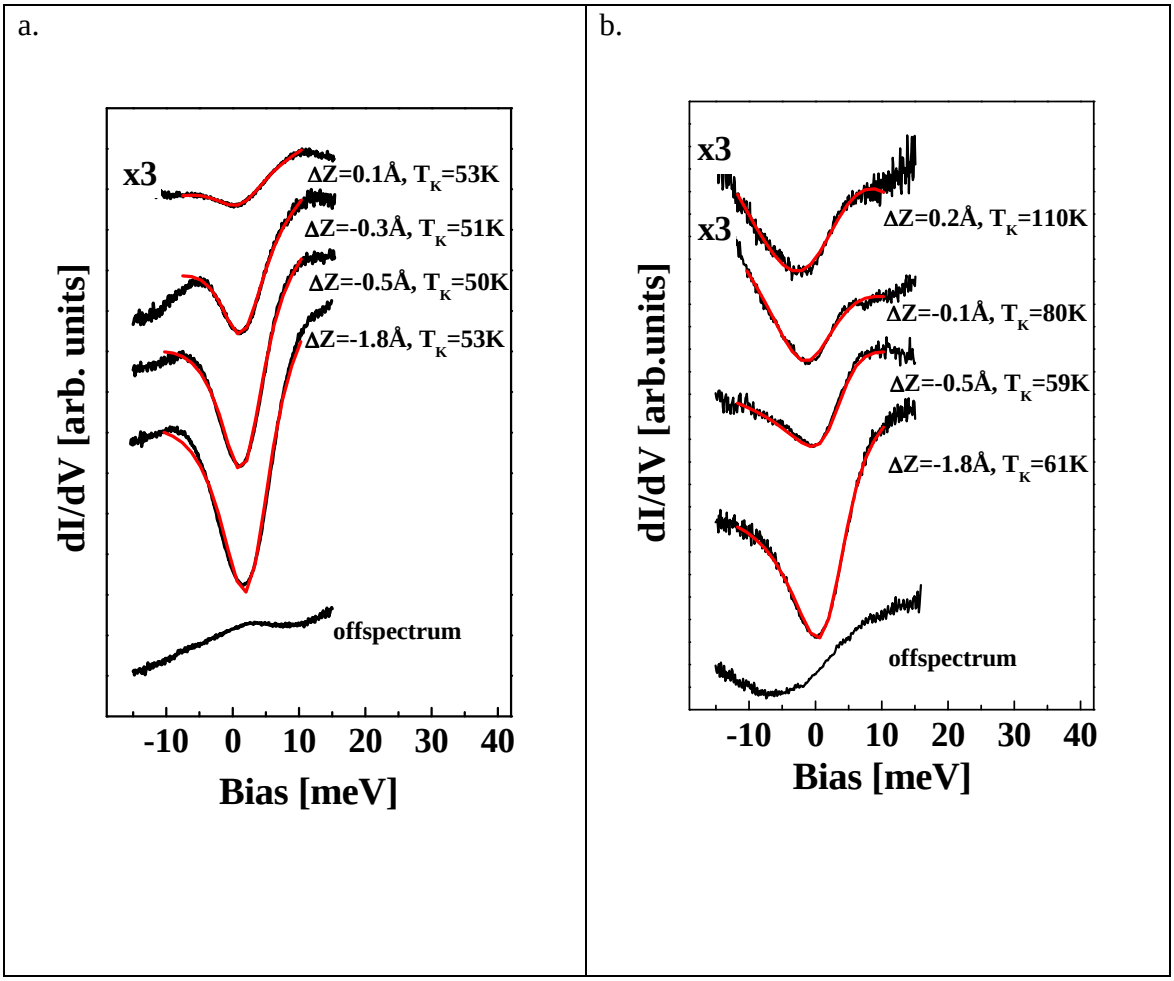

Fig. EPAPS 1: Tip contributions in the dI/dV spectra for isolated Co atoms on a Cu(111) surface. The Kondo resonance at different tip-substrate distances ΔZ from tunneling to point contact is measured with two different scanning tunneling tips: a) a spectroscopic featureless tip; b) with a tip showing a non constant dI/dV spectrum in the energy range of the Fermi level (off-spectrum). The width of the Kondo resonance is constant in the first case at all the given tip-sample distances. In panel b), the observed width of the Kondo resonance increases while reducing the tip-sample distance. This indicates that the tip contributions to the spectra are not negligible and contribute more at reduced distances. All the curves are normalized to the tunneling current at the tip height location. A vertical offset has been added for a better visualization.