Controlling the Kondo Effect in CoCu\textsubscript{n} Clusters Atom by Atom

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Clusters containing a single magnetic impurity were investigated by scanning tunneling microscopy, spectroscopy, and \textit{ab initio} electronic structure calculations. The Kondo temperature of a Co atom embedded in Cu clusters on Cu(111) exhibits a non-monotonic variation with the cluster size. Calculations model the experimental observations and demonstrate the importance of the local and anisotropic electronic structure for correlation effects in small clusters.

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Nanometer scaled electronic devices require the understanding and the control of electron behavior, in particular of correlation effects, at the atomic scale. Experimental techniques such as scanning tunneling microscopy (STM) and spectroscopy and angle-resolved photoemission demonstrate the relevance of many-body phenomena beyond standard band theory\textsuperscript{1}. In many cases, especially for compounds of \textit{d} and \textit{f} elements, strong electron correlations should be taken into account even for a qualitative description of electron energy spectra and physical properties\textsuperscript{2}. The Kondo effect, which is related to the resonant scattering of conduction electrons by quantum local centers, is one of the key correlation effects in condensed matter physics\textsuperscript{3}. It arises from the interaction of a single localized magnetic moment with a continuum of conduction electrons and results in a sharp Abrikosov-Suhl resonance of the local impurity spectral function at the Fermi level and below a characteristic Kondo temperature, \(T_K\)\textsuperscript{3}. Originally detected as a resistance increase below \(T_K\) of materials with dilute magnetic impurities, this many-body phenomenon has been observed for semiconductor quantum dots\textsuperscript{4,5} and for atoms\textsuperscript{6,7,8,9} and molecules\textsuperscript{10} at surfaces. Whereas the understanding of correlation phenomena of bulk materials and single impurities has made significant progress much less is known about these effects in structures such as clusters where typical dimensions are on an atomic scale. STM offers unique opportunities to fabricate such structures by manipulation of single atoms and a few attempts have been made to achieve a degree of control over the electronic\textsuperscript{11,12,13} and magnetic structure\textsuperscript{14,15} of atoms and clusters on surfaces.

Here we show that the Kondo effect of a magnetic impurity does not simply scale with the number of nearest neighbors. Rather, the local and anisotropic electronic structure at the impurity site is important for correlations in atomic scale structures, where "each atom counts"\textsuperscript{16}. We investigate the evolution of the Abrikosov-Suhl resonance induced by a Co atom adsorbed on Cu(111) as we change the number of nearest neighbor Cu atoms. A non-monotonic behavior of the Kondo temperature with the cluster size is at variance with bulk models which are typically invoked to interpret the Kondo effect of a single adsorbed atom (adatom). Scanning tunneling spectroscopy measurements and \textit{ab initio} calculations clearly reveal that the Kondo effect in atomic scaled clusters depends crucially on their detailed geometric structure and thus on the local density of conduction electron states at the magnetic site.

Experiments were performed with a home-made scanning tunneling microscope operated at 7 K and in ultrahigh vacuum with a base pressure of 10\textsuperscript{-9} Pa. Tungsten tips and Cu(111) surfaces were prepared by argon ion bombardment and annealing. While single Co atoms were deposited onto the cold surface using an electron beam evaporator and an evaporant of 99.99\% purity, single Cu atoms were transferred from the tip as previously reported\textsuperscript{[17]}. The individual atoms were chemically identified by the presence (Co) or absence (Cu) of the Abrikosov-Suhl resonance. Clusters consisting of a single Co atom and several Cu atoms\textsuperscript{13,18} were fabricated by atom manipulation with the microscope tip. Spectroscopy was performed by a state-of-the-art lock-in technique.

Figures 1(a)-(e) show a series of constant-current STM images, which illustrates fabrication of a CoCu\textsubscript{n} cluster [Figs.1(a), (b)] and dimensions of CoCu\textsubscript{n} (\(n = 1,\ldots,4\)) clusters [Figs.1(b)-(e)]. In STM images acquired at a sample voltage of 100 mV Co atoms appear higher than Cu atoms [Fig.1(a)], and thus an additional means of discriminating the adatom species is provided. The stick-and-ball models of the clusters used for the calculations are presented in Fig.1(f). Spectroscopy of the differential conductance (\(dI/dV\)) performed with the tip positioned above the cluster center reveals an unoccupied state whose energy decreases with increasing number of Cu atoms [squares in Fig.1(g)]. Our calculations show that this resonance is of \(p_x\) character and are in agreement with experimental data [circles in Fig.1(g)]. This resonance likewise serves as an indicator of the cluster...
Figure 1: (Color online) Scanning tunneling microscopy images and resonance energies of CoCuₙ clusters acquired at 7 K. (a) STM images of single Co and Cu atoms adsorbed on Cu(111) prior to fabricating CoCuₙ clusters. (b) - (e) Sequence of STM images showing CoCuₙ (n = 1,..., 4) clusters. The same lateral and height scale was used for each image. Images were acquired at a sample voltage of 100 mV and a tunneling current of 0.1 nA. (f) Stick-and-ball models of fully relaxed adsorption structures of CoCuₙ (n = 0,..., 4) on Cu(111). (g) Experimental energy of unoccupied cluster state versus the cluster size. The size of the symbols (squares) corresponds to the uncertainty of the energies. Calculated energies are depicted as circles.

Composition and size.

Figure 2 shows a sequence of dI/dV spectra acquired on a single Co atom (lower curve, n = 0) and above the center of CoCuₙ clusters with n ranging between 1 and 4. Starting from a sharp indentation of the differential conductance close to the Fermi level (sample voltage V = 0 mV) which is the spectroscopic signature of the single-Co Kondo effect on Cu(111), the dI/dV curve broadens appreciably upon adding two Cu atoms to the Co atom. Surprisingly, upon increasing the number of hybridizations to three and four Cu atoms, dI/dV spectra exhibit a sharpening of the resonance again in contrast with the monotonic behaviour of the unoccupied pₓ-like state with the number of copper atoms [Fig. 1(g)].

To quantify the broadening of the resonances at the Fermi level we described experimental data by a Fano line shape [19]:

\[
\frac{dI}{dV} \propto \frac{(q + e)^2}{1 + e^2}
\]

with q the asymmetry parameter of the Fano theory and \(e = (eV - \epsilon_K)/(k_B T_K)\) where –e denotes the electron charge, V the sample voltage, \(\epsilon_K\) the resonance energy, and \(k_B\) Boltzmann’s constant. The profiles of Fano line shapes according to Eq. 1 and fitted to dI/dV data are presented as solid lines in Fig. 2. The striking behavior of broadening and sharpening of the Abrikosov-Suhl resonance with increasing number of Cu atoms is reflected by the Kondo temperature \(T_K\) which we plotted in Fig. 3(a). While the single Co adatom exhibits \(T_K = (61 \pm 4) \text{K}\), which is in agreement with a previous publication [9], for CoCu₂ we find \((326 \pm 30) \text{K}\) which then decreases again to \((43 \pm 6) \text{K}\) for CoCu₄. Figure 3(b) shows the evolution of the asymmetry parameter with the cluster size. For n = 0, 1, 2 the asymmetry parameter varies weakly around 0.1. It increases steeply by \(\approx 100\%\) upon adding a third Cu atom. Kondo temperatures and asymmetry parameters for the various clusters are summarized in Table I.

The peculiar behavior of the Kondo resonance with cluster size is at variance with the monotonic dependence

![Figure 2](image2.png)

**FIG. 2:** (Color online) Spectroscopy of the differential conductance (dI/dV) of CoCuₙ clusters around the Fermi level performed at 7 K. The spectroscopic feature is the Abrikosov-Suhl resonance induced by the Kondo effect. Solid lines depict fits of a Fano line shape (Eq. 1) to experimental data. Prior to spectroscopy the tunneling gap was set at 30 mV and 1 nA. Spectra for n = 1, 2, 3, 4 are vertically offset by 5, 10, 20, 25 nS, respectively.

<table>
<thead>
<tr>
<th>n</th>
<th>(T_K) (K)</th>
<th>q</th>
<th>(T_K) (K)</th>
<th>q</th>
</tr>
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<tr>
<td>0</td>
<td>61 ± 4</td>
<td>0.09 ± 0.03</td>
<td>52 ± 4</td>
<td>0.12 ± 0.01</td>
</tr>
<tr>
<td>1</td>
<td>142 ± 10</td>
<td>0.12 ± 0.03</td>
<td>204 ± 12</td>
<td>0.03 ± 0.01</td>
</tr>
<tr>
<td>2</td>
<td>326 ± 30</td>
<td>0.07 ± 0.03</td>
<td>288 ± 3</td>
<td>0.01 ± 0.01</td>
</tr>
<tr>
<td>3</td>
<td>200 ± 15</td>
<td>0.22 ± 0.04</td>
<td>221 ± 18</td>
<td>0.13 ± 0.01</td>
</tr>
<tr>
<td>4</td>
<td>43 ± 6</td>
<td>0.22 ± 0.04</td>
<td>79 ± 3</td>
<td>0.33 ± 0.01</td>
</tr>
</tbody>
</table>

**Table I:** Experimental and calculated Kondo temperatures \(T_K\) and asymmetry parameters (q) for clusters CoCuₙ. \(T_K\) and q were extracted from fits of the Fano line shape (Eq. 1) to measured Kondo resonances shown in Fig. 2. Experimental uncertainty margins correspond to standard deviations obtained by a statistical analysis of a variety of fits. Calculated \(T_K\) and q are the arithmetic mean of values obtained by a Gaussian broadening of the sp local density by 100 meV and 50 meV. The uncertainty margins reflect the deviations of the arithmetic mean from data obtained by 100 meV and 50 meV broadening.
of $T_K$ on the average hybridization strength expected from bulk models of the Kondo effect. Theoretical approaches to the Kondo effect of magnetic impurities on surfaces consider the importance of bulk [20, 21] and surface [22, 23, 24] states in the scattering of electron waves at the magnetic impurity site. Recent experiments with Co adatoms on Cu(100) [9], which does not host any surface state close to the Fermi level [25], or on Cu(111) but in the vicinity of atomic surface steps that affect the surface states [26] have indicated the importance of bulk rather than surface states for the Kondo effect. In this situation, *ab initio* electronic structure calculations which are not restricted by specific model assumptions can be very useful. Here, we perform accurate calculations of the local electronic structure of clusters on the copper surface.

The Kondo temperature for a single magnetic impurity can be estimated as

$$T_K \approx W \sqrt{|J N(E_F)|} \exp \left( -\frac{1}{|J N(E_F)|} \right)$$  \hspace{1cm} (2)

where $W$ is the conduction ($s$) electron bandwidth, $J$ the $s$-$d$ exchange integral, and $N(E_F)$ the density of states at the Fermi energy $E_F$ [3]. Since the $s$-$d$ exchange interaction is local, $N(E_F)$ in Eq.2 is the local density of states of conduction electrons at the magnetic atom.

The asymmetry parameter, $q$, is also determined by the local electronic structure. In a simple model $q$ may be expressed as

$$q = \frac{\gamma + \text{Re} G(E_F)}{\text{Im} G(E_F)}$$  \hspace{1cm} (3)

where $G$ is the local Green’s function of the conduction electrons at the impurity site and $\gamma$ measures the ratio of the coupling of the scanning tunneling microscope tip to conduction electron states and to the strongly localized Co $d$ states [27].

To realistically describe the CoCu$_n$ clusters on Cu(111) we calculated their electronic and structural properties by means of density functional theory using the generalized gradient approximation to the exchange correlation potential [28]. For solving the resulting Kohn-Sham equations accurately, the Vienna Ab Initio Simulation Package [29] with the projector augmented wave basis sets [30, 31] and 350 eV as plane wave cut-off have been used. We modeled the CoCu$_n$ structures using 4 x 3 supercells of Cu(111) slabs containing up to 7 Cu layers. These structures have been fully relaxed with the requirement that all forces are less than 0.2 eV nm$^{-1}$ and
were then used to calculate the local density of states. The supercell Brillouin zone integrations for obtaining the local density of states have been performed using the tetrahedron-method on 6 x 6 k meshes with subsequent 50 - 100 meV Gaussian broadening. Below, we use both, 50 and 100 meV smearing, to provide an uncertainty margin for the derived Kondo temperatures and asymmetry parameters.

The relaxed structures [Fig.1(f)] show that the distance of the Co atom to the Cu surface increases monotonically upon adding Cu atoms to the cluster. However, the local electronic structure at the Fermi level and at the Co site varies in a non-monotonic way with increasing number of Cu atoms. The substrate conduction band states extend to the Co adatom site where they interact with localized Co 3d electrons. This interaction is quantified by the Co sp-projected local density of states, \( N(E) \), which is shown in Figs. 4(a) and 4(b). The dependence of \( G(E_F) \) on the number of Cu atoms is non-monotonic [see the close-up view around \( E_F \) in Fig. 4(b)] and leads, according to Eq. 2, to the experimentally observed non-monotonic behavior of the Kondo temperature (Fig. 3). We used \( W = 20 \text{ eV} \) and \( J = 1.3 \text{ eV} \) as fitting parameters. Moreover, with \( \gamma = 0.22 \text{ eV}^{-1} \) in Eq. 3 the variation of \( G(E_F) \) with the number Cu atoms also reproduces the non-monotonic trend of \( q \) observed in the experiments [Fig. 3(b)]. Figure 4(c) shows the evolution of unoccupied resonance energies with the number of Cu atoms. The resonances appear as peaks in the calculated \( p_x \)-projected local density of states whose energies show the same monotonic behavior as in the experiment [Fig. 1(g)].

The non-monotonic dependence of \( N(E_F) \) on the number of Cu atoms surrounding the Co atom is related to the specific nature of chemical bonds in the system. Since localized d orbitals of Co atoms are strongly anisotropic and form well-defined directional bonds the degree of their hybridization with Cu atoms is determined by the whole geometry of the cluster rather than by just the coordination number.

In summary, we have shown that the Kondo effect in clusters is but depends crucially on their detailed geometrical structure. Atom by atom manipulation changes the local density of conduction electron states at the magnetic site and thus varies the Kondo temperature in rather broad limits. The results demonstrate that electron correlations may be tuned in atomic-scale structures.

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