

Two-Site Kondo Effect in Atomic Chains

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Linear CoCu_nCo clusters on $\text{Cu}(111)$ fabricated by atomic manipulation represent a two-site Kondo system with tunable interaction. Scanning tunneling spectroscopy reveals oscillations of the Kondo temperature T_K with the number n of Cu atoms for $n \geq 3$. Density functional calculations show that the Ruderman-Kittel-Kasuya-Yosida interaction mediated by the Cu chains causes the oscillations. Calculations find ferromagnetic and antiferromagnetic interaction for $n = 1$ and 2, respectively. Both interactions lead to a decrease of T_K as experimentally observed.

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Magnetic atoms with partially filled d or f shells induce strong electron correlations, which cause spectacular effects such as Mott metal-insulator phase transitions, heavy-fermion behavior or the occurrence of high temperature superconductivity. The rich physics of these systems is due to the interplay of local and nonlocal correlation effects. Local correlations are due to Coulomb interaction which makes the probability of an electron to hop into an unoccupied d or f orbital at a site i depend on the number of electrons already present at that site. Nonlocal correlations arise from electrons propagating from one site i to another site j with Coulomb scattering at both sites. In this way, the Ruderman-Kittel-Kasuya-Yosida (RKKY) interaction [1] can cause magnetic correlations between distant atoms and its interplay with (local) Kondo physics is believed to be responsible for magnetic instabilities in heavy-fermion systems.

Two interacting magnetic atoms are the smallest solid state structure to display nonlocal magnetic phenomena due to these correlations. They are consequently an important model system and may also be viewed as a keystone in a bottom-up approach to magnetic nanotechnology. In single-impurity systems, correlations between delocalized band electrons and more localized electrons at the impurity define a characteristic low-energy scale referred to as Kondo temperature T_K , and manifest themselves as an Abrikosov-Suhl resonance of width $k_B T_K$ (k_B : Boltzmann's constant) near the Fermi level. Interactions between two impurities may alter this energy scale and in the limit of strong interactions lead to new regimes including ferromagnetically locked impurity spins or an interimpurity singlet [2,3].

In this work the characteristic low-energy scale is explored as a function of the interaction between two impurities. A Co atom on a $\text{Cu}(111)$ surface is connected to a second Co atom by a chain of Cu atoms. By evaluating the widths of the Abrikosov-Suhl resonances from scanning tunneling spectra we find that T_K is significantly lower for short CoCu_nCo ($n = 1, 2$) than for longer chains ($3 \leq n \leq 6$). Starting from $n = 3$, T_K exhibits even-odd oscillations with the number of Cu atoms. Combining density functional theory (DFT) and perturbative renormalization group (RG) calculations we show that the observed behavior is due to magnetic interactions between the Co adatoms. The observed oscillations of T_K are shown to result from the RKKY interaction mediated by the Cu chains. Overall, both ferromagnetic and antiferromagnetic exchange interactions between the impurities are shown to reduce T_K compared to the single-impurity Kondo scale \tilde{T}_K .

A few scanning tunneling microscope (STM) experiments previously discussed magnetic interactions between individual adsorbed atoms (adatoms). The magnetic hysteresis of two interacting Co atoms on a $\text{Pt}(111)$ surface was investigated as a function of the interatomic distance [4]. Kondo physics was not addressed in that work. The antiferromagnetic coupling between a Kondo Co atom and an unscreened Fe atom on Cu_2N surface induced a splitting of the Kondo resonance similar to Kondo splitting in an external magnetic field [5]. One Co adatom separated by a few Cu layers from an entire magnetic Co film can be similarly understood in terms of single-impurity Kondo physics [6]. In both cases, none of the quantum phase transitions associated with the two-impurity Kondo problem [7] can arise. A disappearance of the Kondo effect or a

reduction of T_K in small Co_2 and Ni_2 clusters have been reported [8,9]. Moreover, the Kondo effect of two Ni atoms on Au(111) was found to be fully developed as soon as the Ni atoms were not in nearest-neighbor positions [9]. Finally, a broadening of the Abrikosov-Suhl resonance has been extracted from tunneling spectra of Co atoms in next-nearest-neighbor positions and used to determine their exchange interaction E_{ex} [10]. However, the method used in Ref. [10] to relate T_K and E_{ex} has been questioned [11]. While in these cases the interaction between magnetic impurities was short-ranged and mediated by the substrate or by direct contact of the magnetic atoms, an intermediate chain of nonmagnetic atoms may affect the interaction [12]. The present work focuses on the impact of such a chain on the Kondo effect. For the first time the long-range interaction of two impurities is explored over the entire range from weakly coupled Kondo impurities to the regime where the interimpurity exchange coupling and \tilde{T}_K are of the same order of magnitude.

The experiments were performed with a STM operated at 7 K and 10^{-9} Pa. Cu(111) surfaces and chemically etched W tips were prepared by Ar^+ bombardment and annealing. Single Co atoms were deposited at ≈ 10 K using an electron beam evaporator while single Cu atoms were transferred from the tip to the sample [13]. The adatoms were chemically identified by the presence (Co) or absence (Cu) of the Abrikosov-Suhl resonance. Spectroscopy of the differential conductance (dI/dV) was performed by a lock-in technique using a modulation amplitude of 1 mV_{rms}. Only tips which reproduced the known spectrum of a single Co adatom were used.

Linear clusters of Co and Cu atoms [14–16] were fabricated with the STM tip by first assembling Cu_n chains along the close-packed $[1\bar{1}0]$ direction and then attaching Co atoms (Fig. 1, left column). For $n \geq 3$, Co atoms are readily discriminated from Cu atoms by their larger apparent height. The right column of Fig. 1 shows dI/dV spectra (dots) acquired above the Co atoms of each CoCu_nCo chain. Spectra acquired at the two Co atoms were virtually identical. The Abrikosov-Suhl resonance appears as an indentation of the dI/dV signal around zero voltage and appreciably broadens from CoCuCo to CoCu_3Co . To quantify its width, the spectra were fit by a Fano line [17], $dI/dV \propto (q + \epsilon)^2 / (1 + \epsilon^2)$ (black line). Fit parameters were the asymmetry parameter q and $\epsilon = (eV - \epsilon_K) / (k_B T_K)$ (V : sample voltage, ϵ_K : resonance energy). While $q \approx 0.1$ and $\epsilon_K \approx 2$ meV are rather independent of the number of Cu atoms, T_K exhibits a pronounced variation (Fig. 2). T_K nearly doubles from $n = 1$ ($T_K \approx 46$ K) to $n = 2$ (≈ 79 K), increases further to ≈ 108 K for CoCu_3Co , and then oscillates ($n = 4$: ≈ 93 K, $n = 5$: ≈ 110 K, $n = 6$: ≈ 91 K). The maxima of the oscillation match the Kondo temperature of a Co atom at the end of CoCu_3 and CoCu_4 chains ($\tilde{T}_K = 110$ K), which approximate a CoCu_∞ chain (dashed line in Fig. 2).

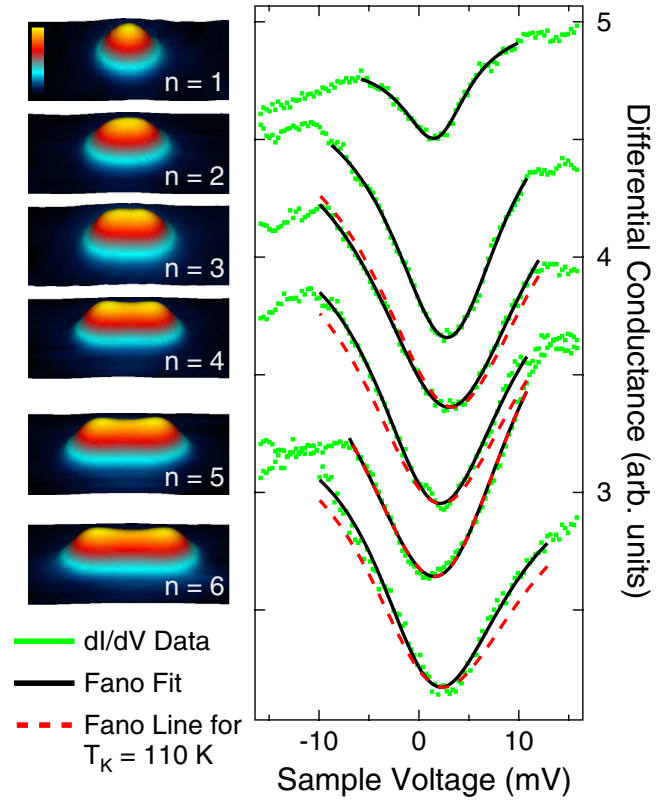


FIG. 1 (color online). Left: Pseudo-three-dimensional representations of constant-current STM images ($38 \text{ \AA} \times 21 \text{ \AA}$) of linear CoCu_nCo clusters ($n = 1 \dots 6$). Right: dI/dV spectra recorded above a Co atom of the chains. Green dots are experimental data, solid lines indicate Fano line shapes fit to the data. The dashed lines are Fano lines for $T_K = 110$ K.

To interpret the evolution of T_K a first-principles description of the CoCu_nCo chains on Cu(111) has been developed. DFT calculations were performed using the Vienna *ab initio* simulation package [18] with the implemented Projector Augmented Waves basis sets [19,20] and employing a generalized gradient approximation (GGA) [21] to the exchange correlation potential. The surface

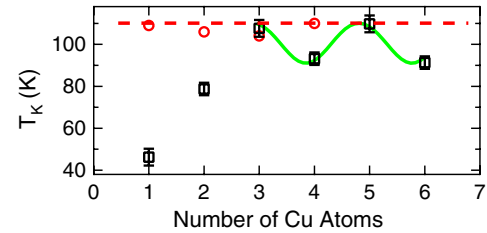


FIG. 2 (color online). T_K of Co atoms in CoCu_nCo chains as a function of n (squares). A dashed line indicates $\tilde{T}_K = 110$ K of a single Co adatom attached to the end of a Cu_3 or Cu_4 chain. Circles (red) indicate calculated *single-impurity* Kondo temperatures, which would be expected for CoCu_nCo chains in the absence of magnetic Co-Co interactions. The sinusoidal line is a fit to data in the RKKY interaction regime with calculated periodicity.

was modeled by (3×9) Cu(111) supercells with slab thicknesses of three to six layers and the CoCu_nCo chains oriented along the $[1\bar{1}0]$ direction. The Kondo physics observed in the experiments is governed by Co $3d$ electrons which are highly sensitive to their atomic environment [16]. Therefore, both adatoms and first surface layer atoms were relaxed until the forces fell below 0.02 eV \AA^{-1} for each atom.

First, we show that *single-impurity* physics cannot explain the experimental variation of T_K . Using the Co hybridization functions obtained from DFT in a RG approach we estimated the variation of T_K with cluster size due to single-impurity effects like variations in the local density of states at the Co site [22]. Extrapolating from $\tilde{T}_K = 110 \text{ K}$ for CoCu_3 and CoCu_4 to the CoCu_nCo chains yields variations of T_K (Fig. 2, circles) which are much smaller than experimentally observed (Fig. 2, squares) and do not even follow the trend of the experimental data.

Because of the reduced coordination Cu atoms within the chain move by 0.16 to 0.23 \AA towards the Cu(111) surface, which corresponds to 8 to 11% of the (111) interlayer spacing. Co atoms at the ends of the chain move by 0.31 to 0.33 \AA toward Cu(111). These relaxations have a significant influence on the magnetic coupling between the Co atoms. This becomes clear from calculations of total energies of a CoCuCo chain for ferromagnetic ($\uparrow\uparrow$) and antiferromagnetic ($\uparrow\downarrow$) spin orientations with and without geometric relaxation. The resulting exchange interaction energy, $E_{\text{ex}} = E_{\uparrow\downarrow} - E_{\uparrow\uparrow}$, is $14 \pm 6 \text{ meV}$ for relaxed CoCuCo chains, while it is significantly smaller $|E_{\text{ex}}| \leq 1 \text{ meV}$ without relaxations. From a calculation within the local density approximation (LDA), $E_{\text{ex}} \approx 40 \text{ meV}$ was reported for the unrelaxed chain [12]. For relaxed CoCu_2Co chains we find $E_{\text{ex}} = -17 \pm 3 \text{ meV}$, which is close to an earlier LDA result [12] and our GGA result $E_{\text{ex}} \approx -20 \text{ meV}$ for the unrelaxed chain. The signs of E_{ex} indicate ferro- and antiferromagnetic coupling between the Co atoms in CoCuCo and CoCu_2Co chains, respectively.

Despite the ferromagnetic Co-Co coupling in the CoCuCo chain an Abrikosov-Suhl resonance with $T_K = 46 \text{ K}$ is observed in the experiments, which may appear surprising. The interplay of interimpurity coupling, $H = -J\vec{S}_1 \cdot \vec{S}_2$, and Kondo screening has been theoretically addressed in terms of two-site spin-1/2 Kondo models [2,3]. For ferromagnetic interimpurity exchange interaction, $J > 0$, dominating over the single-impurity Kondo energy scale, $k_B\tilde{T}_K \ll J$, locking of the two spins to a total spin, $S_1 + S_2 = 1$, followed by a spin-1 Kondo effect has been predicted [2]. In this case, the Kondo temperature is reduced, $T_K \approx k_B\tilde{T}_K^2/J$ [23]. With $T_K = 46 \text{ K}$ and $\tilde{T}_K = 110 \text{ K}$, J is estimated as 23 meV . As J is related to $E_{\text{ex}} = 14 \pm 6 \text{ meV}$ by a factor of the order of 1, the experimentally observed reduction of \tilde{T}_K is well in line with E_{ex} as obtained from our calculations [24]. Consequently, theory

and experiment consistently suggest that CoCuCo is in the crossover region between two independent and two ferromagnetically locked Kondo impurities [2,3], where a narrowed rather than a completely suppressed Abrikosov-Suhl resonance is found.

In the case of CoCu_2Co , where the Co atoms couple antiferromagnetically, our GGA calculations show that $|E_{\text{ex}}| \approx 2k_B\tilde{T}_K$. In a particle-hole-symmetric case, the two-site spin-1/2 Kondo model exhibits a quantum critical point at $J \approx 2.2k_B\tilde{T}_K$ separating ground states with an antiferromagnetically locked interimpurity singlet from two Kondo-screened impurities [3]. In systems without particle-hole symmetry, the quantum critical point is replaced by a crossover region, where the spectral weight of the Abrikosov-Suhl resonance is continuously reduced and evolves into a pseudogap feature [25–28]. In this crossover region, there are two energy scales, $T_L < T_H$, characterizing the spin-fluctuations and the quasiparticle excitation spectra of the system [25,26,28]. The lower scale, T_L , gives rise to the sharpest and most pronounced feature in the spectral function at the Fermi level [26] and characterizes the onset of local Fermi liquid behavior [28]. Hence, $k_B T_L$ should appear as the width of the experimentally observed Abrikosov-Suhl resonance and we refer to $T_L = T_K$ as the Kondo temperature of the two-impurity system. As $T_L < \tilde{T}_K$ [25,26,28], a narrowed Abrikosov-Suhl resonance as observed experimentally (Figs. 1 and 2) is well in line with this crossover regime. The results for $n = 1, 2$ prove that positive and negative exchange interactions lead to $T_K < \tilde{T}_K$ [29,30].

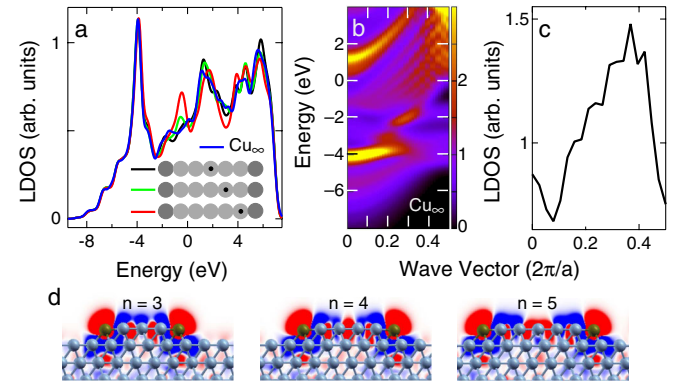


FIG. 3 (color online). (a) Local density of states (LDOS) of Cu $4s$ and $4p$ orbitals in a CoCu_5Co chain and in an infinitely long Cu chain (Cu_∞) on Cu(111). Cu sites at which the LDOS was evaluated are indicated by dots. (b) LDOS of Cu_∞ on Cu(111) versus energy and wave vector along the chain direction. (c) Cross section of (b) at $E = 0 \text{ eV}$. (d) Relaxed CoCu_nCo ($3 \leq n \leq 5$) chains with calculated magnetization density for ferromagnetically aligned Co spins. Light (red) and dark (blue) colors indicate up and down orientations, respectively. Away from the Co impurity the induced magnetization density is largest around the chain atoms. Therefore, the major contribution to the RKKY interaction between the Co atoms is mediated by the Cu chains.

To understand the oscillations of T_K for $n \geq 3$ the electronic structure of an infinite Cu chain (Cu_∞) on Cu(111) is considered. Its structural relaxations (i.e. 0.2 Å downward relaxation of the chain atoms) and its local density of states (LDOS) are similar to those observed from CoCu_nCo for $n \geq 3$. Cu atoms that are no direct neighbors of Co atoms exhibit a similar LDOS as Cu atoms in Cu_∞ [Fig. 3(a)]. Therefore, the Fermi wave vector k_F , which determines LDOS oscillations of the chains and the RKKY interaction, has been calculated from the band structure of Cu_∞ . Figure 3(b) shows the energy- and momentum-resolved LDOS of conduction electrons of Cu_∞ . The band of unoccupied states starting at $E = 1.2$ eV at $k = 0$ has been measured in Refs. [14,31] and does not contribute spectral weight at the Fermi energy ($E_F = 0$ eV). At E_F [Fig. 3(c)] spectral weight is suppressed for $k_F < 0.1(2\pi/a)$ [a : Cu(111) lattice constant, $a = 2.57$ Å] and exhibits a maximum at $\approx 0.37(2\pi/a)$. Hence, Co–Co RKKY interactions and LDOS resonances at E_F are expected to oscillate with a wave vector $2k_F \approx 0.74(2\pi/a)$ which by subtracting a reciprocal lattice vector is identical with $-0.26(2\pi/a)$ and corresponds to a direct space period of $\approx 3.8a$. This period can be clearly seen in Fig. 3(d) as an oscillatory magnetization density along the Cu chains. The period expected for T_K , however, is different. In the limit of weak RKKY interaction, the correction to the Kondo temperature reads $\tilde{T}_K^2 - T_K^2 \approx E_{\text{ex}}^2/k_B^2$ [22,29,30]. Given that $E_{\text{ex}}^2 \propto \sin^2(2k_Fna)$ the spatial periodicity is reduced to $\approx 1.9a$, which corresponds well to the even-odd oscillations of T_K observed in the experiments.

In summary, linking two Co atoms by a chain of Cu atoms nonlocal correlations between two Kondo impurities have been probed. The interimpurity interaction is shown to lower the Kondo temperatures in short clusters and leads to RKKY induced oscillations at larger chain lengths. A reduction of the Kondo temperature independent of the sign of the interimpurity exchange interaction is found. These effects observed from a two-impurity system may find a counterpart in crystalline solids as indicated by model studies of the double Bethe lattice [32].

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 [23] This is a limiting case of footnote 10 in [2] for $k_F R \gg 1$ or $k_F R \approx n\pi$ with integer nonzero n .
 [24] This very good agreement should be considered only qualitatively, as $T_K \approx k_B \tilde{T}_K^2 / J$ has been derived for $J \gg k_B \tilde{T}_K$, while here we have $J \approx 2k_B \tilde{T}_K$.
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