Two-Site Kondo Effect in Atomic Chains

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Linear CoCuₙCo clusters on Cu(111) are fabricated by means of atomic manipulation. They 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 interaction which makes the probability of an electron to

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Co2 and Ni2 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 \[3\]. 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 $E_{\text{ex}}$ \[10\]. However, the method used in Ref. \[10\] to relate $T_K$ and $E_{\text{ex}}$ 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 $T_K$ 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 $\approx 10$ 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 mVrms. 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 by manipulation with the STM tip by first assembling Cu$_n$ chains along the close-packed [110] 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 Cu$_n$Co 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$_3$Co. 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 $\epsilon = (eV - \epsilon_K)/(k_BT_K)$ ($V$: sample voltage, $\epsilon_K$: 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 $n = 2$ ($\approx 79$ K), increases further to $\approx 108$ K for CoCu$_3$Co, and then oscillates ($n = 4$: $\approx 93$ K, $n = 5$: $\approx 110$ K, $n = 6$: $\approx 91$ K). The maxima of the oscillation match the Kondo temperature of a Co atom at the end of CoCu$_3$ and CoCu$_4$ chains ($T_K = 110$ K), which approximate a CoCu$_\infty$ chain (dashed line in Fig. 2).

FIG. 1. (Color online) Left: Pseudo-three-dimensional representations of constant-current STM images (38 $\times$ 21 $\AA$) of linear CoCu$_n$Co clusters ($n = 1 \ldots 6$). Right: $dI/dV$ spectra recorded above the Co atoms 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, which corresponds to a Co adatom attached to a Cu$_4$ chain.

FIG. 2. (Color online) $T_K$ of Co atoms in CoCu$_n$Co chains as a function of $n$ (squares). A dashed line indicates $T_K = 110$ K of a single Co adatom attached to the end of a Cu$_4$ chain. The circles (red) indicate calculated single-impurity Kondo temperatures, which would be expected for CoCu$_n$Co 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.
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 $T_K = 110$ K for CoCu$_3$ and CoCu$_4$ to the CoCu$_n$Co 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.

Due to the reduced coordination Cu atoms within the chain move by 0.16 to 0.23 A 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 A 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 an Abrikosov-Suhl resonance with a Kondo temperature of 110 K, followed by a spin-1 Kondo effect has been predicted \[2\]. In this case, the Kondo temperature is reduced, $T_K \approx k_B T_K/2$. With $T_K = 46$ K and $T_K = 110$ K, $J$ is estimated as 23 meV. As $J$ is related to $E_{ex} = 14 \pm 6$ meV by a factor of the order of one, the experimentally observed reduction of $T_K$ 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 aligned Co spins, where a narrowed rather than a completely suppressed Abrikosov-Suhl resonance is found.

In the case of CoCu$_2$Co, where the Co atoms couple antiferromagnetically, our GGA calculations show that $E_{ex} \approx 2k_B T_K$. In a particle-hole-symmetric case, the two-site spin-1/2 Kondo model exhibits a quantum critical point at $J = 2k_B T_K$ 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 \[25\]. 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 \[25\]. 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 $T_L < T_K$ \[23\], a narrowed Abrikosov-Suhl resonance as observed exper-
mentally (Figs. \[1, 2\]) is well in line with this crossover regime. The results for \( n = 1, 2 \) prove that positive and negative exchange interactions lead to \( T_K < T_K^{\text{ref}} \).

To understand the oscillations of \( T_K \) for \( n \geq 3 \) the electronic structure of an infinite Cu chain (Cu\(_{\infty}\)) 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\(_n\)Co for \( n \geq 3 \). Cu atoms that are no direct neighbors of Co atoms exhibit a similar LDOS as Cu atoms in Cu\(_{\infty}\) [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 CoCu\(_n\)Co for \( n \geq 3 \) and leads to RKKY induced oscillations at larger chain lengths. The period can be clearly seen in Fig. 3(d) as an oscillatory magnetization density along the Cu chains. The period expected for \( T_K \) oscillations is \( \pi/2a \approx 3.5 \text{ Å} \) and exhibits a maximum at \( \pi/2a \approx 2.57 \text{ Å} \) 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 \( 2k_F \approx 0.74(2\pi/a) \) by which subtracting a reciprocal lattice vector is identical with \( -0.26(2\pi/a) \) and corresponds to a direct space period of \( \approx 3.8 \text{ Å} \). 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 \( T_K^2 - T_K^2 \approx E_{\text{cs}}^2/k_B^2 \) [22, 29, 30]. Given that \( E_{\text{cs}}^2 \propto \sin^2(2k_Fa) \) the spatial periodicity is reduced to \( \approx 1.9 \text{ Å} \), 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 proven to quench 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 \( k_F \) \( \sim \) \( n \), \( \pi \) with integer nonzero \( n \).
[24] This very good agreement should be considered only qualitatively, as \( T_K \approx k_B T_k/J \) has been derived for \( J \gg k_B T_k \), while here we have \( J \approx 2 k_B T_k \).
[32] H. Hafermann, M. I. Katsnelson, and A. I. Lichtenstein,