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.

PACS numbers: 68.37.Ef,72.15.Qm,73.20.Fz

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 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 possible 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 $k_B T_K$ 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.

In this work the characteristic low-energy scale is explored as a function of the interaction between two impurities. A Co atom on a 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 CoCuₙCo ($n = 1, 2$) 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 addressed magnetic interactions between individual adsorbed atoms (adatoms). The magnetic hysteresis of two interacting Co atoms on a Pt(111) surface was investigated as a function of the interatomic distance. Kondo physics was not addressed in that work. The antiferromagnetic coupling between a Kondo Co atom and an unscreened Fe atom on Cu₂N surface induced a splitting of the Kondo resonance similar to Kondo splitting of single atom in external magnetic field. 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. In both cases, none of the quantum phase transitions associated with the two-impurity Kondo problem can arise. A disappearance of the Kondo effect or a reduction of $T_K$ in small
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 CoCu$_n$Co to CoCu$_4$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).

To interpret the evolution of $T_K$ a first-principles description of the CoCu$_n$Co 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 was modeled by (3 x 9) Cu(111) supercells with slab thicknesses of three to six layers and the CoCu$_n$Co chains oriented along the [110] direction. The Kondo physics observed in the experiments are governed by Co 3$d$ electrons which are highly sensitive to their atomic interactions.
face, which corresponds to 8 to 11% of the (111) in-

environment. Therefore, both adatoms and first sur-
face layer atoms were relaxed until the forces fell below
0.02 eV Å^{-1} for each atom.

First, we show that single-impurity physics cannot ex-
plain the experimental variation of \( T_K \). Using the Co
hybridization functions obtained from DFT in a RG ap-
proach 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 \[22\]. Extrapo-
lation from \( T_K = 110 \text{ K} \) for CoCu3 and CoCu4 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 Å towards the Cu(111) sur-
face, which corresponds to 8 to 11% of the (111) in-
terlayer spacing. Co atoms at the ends of the chain
move by 0.31 to 0.33 Å toward Cu(111). These relax-
ations have a significant influence on the magnetic cou-
pling between the Co atoms. This becomes clear from
calculations of total energies of a CoCuCo chain for fer-
romagnetic (\( \uparrow\uparrow \)) and antiferromagnetic (\( \uparrow\downarrow \)) spin orien-
tations with and without geometric relaxation. The re-
sulting exchange interaction energy, \( \Delta E_{ex} = E_{\uparrow\uparrow} - E_{\uparrow\downarrow} \),
is 14 ± 6 meV for relaxed CoCuCo chains, while it is
significantly smaller \( \Delta E_{ex} \leq 1 \text{ meV} \) without relaxations.
From a calculation within the local density approxima-
tion (LDA), \( \Delta E_{ex} \approx 40 \text{ meV} \) was reported for the un-
relaxed chain \[12\]. For relaxed CoCu\(_2\)Co chains we find
\( \Delta E_{ex} = -17 \pm 3 \text{ meV} \), which is close to an earlier LDA re-
sult \[12\] and our GGA result \( \Delta E_{ex} \approx -20 \text{ meV} \) for the un-
relaxed chain. The signs of \( \Delta E_{ex} \) indicate ferro- and anti-
ferromagnetic coupling between the Co atoms in CoCuCo
and CoCu\(_2\)Co 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 ap-
pear surprising. The interplay of interimpurity coupling,
\( H = -J \vec{S}_1 \cdot \vec{S}_2 \), and Kondo screening has been theo-
retically 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, \( k_B T_K \ll J \), 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 tem-
perature is reduced, \( T_K \approx k_B \tilde{T}_K/J \) \[24\]. With \( T_K = 46 \text{ K} \)
and \( \tilde{T}_K = 110 \text{ K} \), \( J \) is estimated as 23 meV. As \( J \) is rel-
ated to \( \Delta E_{ex} = 14 \pm 6 \text{ meV} \) by a factor of the order of one,
the experimentally observed reduction of \( T_K \) is well
in line with \( \Delta E_{ex} \) as obtained from our calculations \[24\].
Consequently, theory and experiment consistently sug-
ject that CoCuCo is in the crossover region between two
independent and two ferromagnetically locked Kondo im-
purities \[2, 3\], 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
\( \Delta E_{ex} \approx 2 k_B \tilde{T}_K \). In a particle-hole-symmetric case, the
two-site spin-1/2 Kondo model exhibits a quantum crit-
ical point at \( J \approx 2.2 k_B \tilde{T}_K \) separating ground states
with an antiferromagnetically locked interimpurity sin-
glet from two Kondo-screened impurities \[3\]. In sys-
tems without particle-hole symmetry, the quantum crit-
ical point is replaced by a crossover region, where the
spectral weight of the Abrikosov-Suhl resonance is con-
tinuously 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 \[25, 27, 28\].
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, \( k_B \tilde{T}_L \) 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 \( T_L < T_K \) \[25, 26, 28\], 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 \( T_K < \tilde{T}_K \) [22, 30].

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 \( \mathbf{k}_F \), which determines LDOS oscillations of the chains and the RKKY interaction, has been calculated from the band structure of Cu\(_\infty\). Figure 3(b) shows the energy- and momentum-resolved LDOS of conduction electrons of Cu\(_\infty\). The band of unoccupied states starting at \( E = 1.2 \) eV at \( k = 0 \) has been measured in Refs. [14, 51] 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 \( 2k_F \approx 0.74(2\pi/a) \) by subtracting a reciprocal lattice vector is identical with \( F \frac{a}{2} \approx F \frac{a}{2} = 2\pi/a \) 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 \( T_K^2 - T_K^2 \approx E_{\text{ex}}^2/k_B^2 \) [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 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].

Financial support by the Deutsche Forschungsgemeinschaft through SFB 668, the Innovationsfonds Schleswig-Holstein and FOM (The Netherlands) is acknowledged. We thank A. Rosch for providing his RG code.

[1] M. A. Ruderman and C. Kittel, Phys. Rev. 96, 99 (1954); T. Kasuya, Prog. Theor. Phys. 16, 45 (1956); K. Yosida, Phys. Rev. 106, 893 (1957).
[2] C. Jayaprakash, H. R. Krishnamurthy, and J. W. Wilkins, Phys. Rev. Lett. 47, 737 (1981).
[3] B. A. Jones and C. M. Varma, Phys. Rev. Lett. 58, 843 (1987); B. A. Jones, C. M. Varma, and J. W. Wilkins, ibid. 61, 15 (1988).
[4] J. Zhou, J. Wiebe, S. Lounis, E. Vedmedenko, F. Meier, S. Blügel, P. H. Dederichs, and R. Wiesendanger, Nature Phys. 6, 187 (2010).
[5] A. F. Otte, M. Ternes, S. Loth, C. P. Lutz, C. F. Hirjibehedin, and A. J. Heinrich, Phys. Rev. Lett. 103, 107203 (2009).
[6] T. Uchihashi, J. Zhang, J. Kröger, and R. Berndt, Phys. Rev. B 78, 033402 (2008).
[7] R. Bulla, T. A. Costi, and T. Pruschke, Rev. Mod. Phys. 80, 395 (2008).
[8] W. Chen, T. Jammeala, V. Madhavan, and M. F. Crommie, Phys. Rev. B 60, R8529 (1999).
[9] V. Madhavan, T. Jammeala, K. Nagaoka, W. Chen, J.-L. Li, S. G. Louie, and M. F. Crommie, Phys. Rev. B 66, 212411 (2002).
[10] P. Wahl, P. Simon, L. Diekhöner, V. S. Stepanyuk, P. Bruno, M. A. Schneider, and K. Kern, Phys. Rev. Lett. 98, 056601 (2007).
[11] E. Minamitani, H. Nakashima, W. A. Diño, and H. Kasai, J. Phys. Soc. Jpn. 78, 084705 (2009).
[12] O. O. Brovko, P. A. Ignatiev, V. S. Stepanyuk, and P. Bruno, Phys. Rev. Lett. 101, 036809 (2008).
[13] L. Limot, J. Kröger, R. Berndt, A. Garcia-Lekue, and W. A. Hofer, Phys. Rev. Lett. 94, 126102 (2005).
[14] J. Lagoute, C. Nacci, and S. Fölsch, Phys. Rev. Lett. 98, 146804 (2007).
[15] J. A. Stroscio, F. Tavaazzi, J. N. Crain, R. J. Celotta, and A. M. Chaka, Science 313, 948 (2006).
[16] N. Néel, J. Kröger, R. Berndt, T. O. Wehling, A. J. Lichtenstein, and M. I. Katsnelson, Phys. Rev. Lett. 101, 266803 (2008).
[17] U. Fano, Phys. Rev. 124, 1866 (1961).
[18] G. Kresse and J. Hafner, J. Phys.: Condens. Matter 6, 8245 (1994).
[19] P. E. Blöchl, Phys. Rev. B 50, 17953 (1994).
[20] G. Kresse and D. Joubert, Phys. Rev. B 59, 1758 (1999).
[21] J. P. Perdew et al., Phys. Rev. B 46, 6671 (1992).
[22] See EPAPS Document No. XXX for details of the perturbative RG analysis and the generalization of [29] to the two-impurity Kondo problem.
[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 \( T_K \approx k_B T_K \) has been derived for \( J \gg k_B T_K \), while here we have \( J \approx 2k_B T_K \).
[25] O. Sakai, Y. Shimizu, and T. Kasuya, Sol. State Commun. 75, 81 (1990); O. Sakai and Y. Shimizu, J. Phys. Soc. Jpn. 61, 2333 (1992); 61, 2348 (1992).
[26] O. Sakai, Y. Shimizu, and N. Kaneko, Physica B 186, 323 (1993).
[27] I. Affleck, A. W. W. Ludwig, and B. A. Jones, Phys. Rev. B 52, 9528 (1995).
[28] L. Zhu and J.-X. Zhu, arxiv:1005.5154 (2010).
[29] V. Y. Irkhin and M. I. Katsnelson, Z. Phys. B 75, 67 (1989).
[30] V. Y. Irkhin and M. I. Katsnelson, Phys. Rev. B 56, 8109 (1997).
[31] S. Fölsch, P. Hyldgaard, R. Koch, and K. H. Ploog, Phys. Rev. Lett. 92, 056803 (2004).
[32] H. Hafermann, M. I. Katsnelson, and A. I. Lichtenstein,
Europhys. Lett. 85, 37006 (2009).