Manipulation of the two-site Kondo effect in linear CoCu$_n$CoCu$_m$ clusters

N Néel$^1$, B Shao$^{2,3}$, T O Wehling$^{2,3}$ and J Kröger$^1$

$^1$ Institut fü r Physik, Technische Universität Ilmenau, D-98693 Ilmenau, Germany
$^2$ Bremen Center for Computational Materials Science, University Bremen, D-28359 Bremen, Germany
$^3$ Institute for Theoretical Physics, University Bremen, D-28359 Bremen, Germany

E-mail: nicolas.neel@tu-ilmenau.de

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Abstract

Artificially assembled linear atomic clusters, CoCu$_n$CoCu$_m$, are used to explore variations of the Kondo effect at the two Co sites. For all investigated Cu$_n$ chain lengths ($n = 2, 3, 4$) the addition of a single Cu atom to one edge Co atom of the chain ($m = 0 \rightarrow m = 1$) strongly reduces the amplitude of the Abrikosov–Suhl–Kondo resonance of that Co atom. Concomitantly, the resonance line width is more than halved. On the contrary, the Kondo effect of the opposite edge Co atom remains unaffected. Hybridization together with the linear geometry of the cluster are likely to drive the effect.

Keywords: Kondo effect, Abrikosov–Suhl resonance, scanning tunnelling microscopy, atom manipulation, magnetic atoms, linear clusters, metal surfaces

S Supplementary material for this article is available online

(Some figures may appear in colour only in the online journal)

1. Introduction

The Kondo effect describes the collective screening of an atomic magnetic moment by the conduction electron continuum it is embedded in [1, 2]. This correlated many-body state occurs below a characteristic temperature, the Kondo temperature $T_K$, and represents an archetypical example of local correlations where hopping of a conduction electron to an unoccupied orbital at the impurity site depends on the number of electrons already present at that site via the Coulomb interaction. Adding a second atomic magnetic moment gives rise to non-local correlations due to direct magnetic exchange and indirect Ruderman–Kittel–Kasuya–Yosida (RKKY) [3–5] interactions. These non-local correlations compete with the local Kondo scattering and alter the single-impurity energy scale $k_B T_K$ ($k_B$: Boltzmann constant). Spin singlet or triplet states are conceivable as well as individually screened magnetic moments [6–8].

The spectroscopic signature of the Kondo effect is a resonance in the electron excitation spectrum at the Fermi energy $E_F$ and is referred to as the Kondo [1] or Abrikosov–Suhl [9–11] resonance. Its detection at the single-atom level using spectroscopy of the differential conductance ($dI/dV$, $I$: tunnelling current, $V$: bias voltage) with a scanning tunnelling microscope (STM) [12, 13] represents a milestone in surface physics. The Kondo resonance appears with a Fano line shape [14, 15] in $dI/dV$ spectra, which reflects that spin-conserving tunnelling occurs directly from the tip to the conduction electron continuum and indirectly via the Kondo resonance. The interference of tunnelling electrons in these two paths leads to the characteristic spectroscopic line shape, which is defined by the asymmetry parameter of the Fano theory [14, 15]. The Frota line shape was suggested as a different way of describing the Kondo resonance [16, 17] and successfully applied in experiments [18, 19]. Many-body numerical renormalization group calculations justify the phenomenological Frota line shape [20]. The widths
of Fano and Frota line shapes are related to $T_K$ and differ by a constant factor [18]. A substantial amount of reports on the single-impurity Kondo effect—atoms [21–26] and molecules [27–44, 45]—followed the first observations [12, 13] and are reviewed in parts in, e.g. [46–48].

The details of the Abrikosov–Suhl–Kondo (ASK) resonance line shape were demonstrated to be a subtle probe for magnetic interaction [39, 49–58], hybridization [26, 28–30, 59–63] and density of states (DOS) effects [64–66]. Here, we explore the ASK resonance of Co atoms in CoCu$_m$CoCu$_n$ linear clusters with $dI/dV$ spectroscopy. Unexpectedly, the attachment of a Cu atom to one edge Co atom significantly decreases amplitude and width of the resonance. Changes in the magnetic interaction between the Co atoms as well as hybridization effects alone are not consistent with these observations. While currently model calculations are not available the experimental data hint at the cluster geometry playing an important role in the effect. The presented findings also call for honing theoretical tools to describe experimental Kondo physics.

2. Experiment

Experiments were performed with an STM operated in ultra-high vacuum ($10^{-9}$ Pa) and at 6 K. Cu(1 1 1) surfaces were cleaned by Ar$^+$ bombardment and annealing. Chemically etched W wires (presumably) coated with Cu substrate material served as STM tips. Single Co atoms were deposited at $\approx 8$ K from an electron beam evaporator through openings of the radiation shields of the bath cryostat. Single Cu atoms were transferred from the tip to the surface by controlled tip-surface contacts [67–70]. STM images were recorded at constant current with the bias voltage applied to the sample. Co and Cu atoms on Cu(1 1 1) can be distinguished by their different apparent heights in STM images. For instance, at $V = 30$ mV Co atoms appear $\approx 35\%$ higher than Cu atoms. Spectra of $dI/dV$ were recorded by sinusoidally modulating the bias voltage ($1$ mV$_{\text{rms}}$, 950 Hz) and measuring the first harmonic of the current response of the tunnelling junction with a lock-in amplifier.

3. Results and discussion

The CoCu$_m$CoCu$_n$ chains on Cu(1 1 1) were fabricated atom by atom [71, 72]. After assembling the linear Cu$_n$ cluster, each edge of the chain was decorated by a single Co atom. The intermediate Cu$_n$ wire connecting the two Co atoms at the edges was theoretically predicted [73] and experimentally demonstrated [54] to enhance the magnetic interaction between the Co atoms, which is advantageous for the purpose of the experiments presented here. Additional $m$ Co atoms were then attached to one Co edge atom, continuing the direction of the chain.

Figure 1 shows STM images of all linear clusters considered in this work, $2 \leq n \leq 4$ and $0 \leq m \leq 2$. The clusters are aligned with (1 1 0) crystallographic directions of Cu(1 1 1). In symmetric chains (figures 1(a)–(c)) Co atoms reside at the edges of the atomic chain. Their apparent height is only slightly higher than observed from Cu atoms. The addition of Cu atoms to one Co atom (figures 1(d)–(i)) leads to asymmetric chains, in which the additionally coordinated Co atom appears higher than the rest of the chain atoms signalling a change in the local DOS at this Co site. In the following, this Co atom will be referred to as Co$_0$.

The most important question concerns the evolution of the ASK resonance of the two Co atoms in the chain with the variation of $m$, i.e. with the attachment of additional Cu atoms to one end of the linear cluster. CoCu$_m$Co clusters on Cu(1 1 1) were studied previously for $1 \leq n \leq 6$ [54]. Characteristic changes in the resonance width and, thus, in $T_K$ were rationalized in terms of ferromagnetic ($n = 1$), anti-ferromagnetic ($n = 2$) and RKKY ($n \geq 3$) interactions between the Co atoms [54]. The unexpected trend in the present findings is exemplarily shown in figure 2 for the shortest intermediate Cu chain ($n = 2$) and applies to all other linear clusters investigated (figure S1 and table S1 in supplementary material (available online at stacks.iop.org/JPhysCM/32/055303/mmedia)). In symmetric clusters ($m = 0$, figure 2(a)) both Co edge atoms exhibit an ASK resonance with similar amplitude and width, in agreement with previous observations [54]. Adding a single Cu atom to an edge Co atom ($m = 1$, figure 2(b)) entails a strong modification of the Co ASK resonance line shape (figure 2(b), top). The amplitude nearly vanishes and the width is reduced by more than a factor 2 compared to the symmetric cluster. The ASK resonance of the other edge Co atom (figure 2(b), bottom) stays nearly invariant. The addition of a second Cu atom ($m = 2$, figure 2(c)) does not lead to remarkable changes in the ASK resonance line shape compared to the case of $m = 1$, neither for Co$_0$ nor for Co.

In order to extract quantitative changes in the line shape, the Fano function, $f(V) = a \cdot (q + e)^2/(1 + e^2)$ ($a$: amplitude, $q$: asymmetry parameter, $e = \beta \cdot (eV - \epsilon_0)$ with $1/\beta = k_B T_K$, $e$ the elementary charge and $\epsilon_0$ the resonance energy), riding on a quadratic background was fit to the spectroscopic data. The solid lines in figure 2 depict the results of these fits. A more sophisticated parameterization of the Fano function [74] was not required. Moreover, we have not attempted to use the Frota function for fitting the data [75] since rather than extracting the absolute width of the ASK resonance we are mainly interested in its trend with $m$ and $n$. The widths of Fano and Frota functions are related by a constant factor [18] and are therefore expected to give rise to similar trends.

Figure 3 shows the evolution of $T_K$ as a function of $m$ (figures 3(a) and (b)) and $n$ (figure 3(c)). The Kondo temperature obtained from spectra above Co$_0$ (figure 3(a)) drops strongly upon attaching a single Cu atom. In the shortest chain ($n = 2$) $T_K$ decreases from 85 K to 36 K when $m$ changes from 0 to 1. For the other chains ($n = 3, 4$) the decrease of $T_K$ is similarly pronounced. The addition of a second Cu atom ($m = 2$) does not cause strong variations in $T_K$. In contrast, the Kondo temperature of the opposite Co atom in the cluster is hardly affected (figure 3(b)). All clusters ($2 \leq m \leq 4$) exhibit similar trends. Additionally, an even-odd oscillation of $T_K$ in the number $n$ of Cu atoms is observed for all investigated $m = 0, 1, 2$ (figure
These oscillations are akin to $T_K$ variations reported for even longer intermediate Cu chains [54] and are therefore assigned to the same origin, i.e. to RKKY interactions [54, 76]. It is remarkable—albeit not understood—that for $m = 1, 2$ the oscillation amplitude is larger than for $m = 0$.

The maximum variation of $T_K$ is observed for $m = 2$ where $T_K$ drops from 68 K ($n = 3$) to 25 K ($n = 4$), while $T_K$ changes at maximum from 86 K ($n = 2$) to 98 K ($n = 3$) in the case of $m = 0$. Before discussing these findings we mention that the asymmetry factor $q$ varies between −0.1 and 0.1 for all investigated clusters and does not exhibit a characteristic trend.

Using the data presented in figure 3 the following conclusions may be drawn. The strong reduction of $T_K$ of Co hint at hybridization...
The hybridization of the Co edge atom with an additional Cu atom remains a possible rationale for the observed $T_K$ reduction. To resolve the apparent contradiction with earlier findings for compact CoCu$_n$ clusters (vide supra) the geometry of the cluster must be taken into account. In contrast to compact CoCu$_n$ clusters, the addition of Cu atoms to linear CoCu$_n$Co preserves the linear shape of the cluster. Since the importance of the local and anisotropic electronic structure for correlation effects was unravelled in small clusters [60], the presented results may be explained along these lines.

Additionally, relaxations of the Co adsorption height upon Cu atom attachment may be different from the situation of compact clusters and lead to a different evolution of $T_K$. Relaxations as low as in the pm range were shown to have profound impact on correlation effects [54].

Before concluding, quantum confinement effects shall briefly be discussed. The Shockley surface state of Cu(1 1 1) has significant spectral weight at $E_F$ and, therefore, could influence the ASK resonance. Its Fermi wavelength is $\lambda_F \approx 2.7$ nm [77–79] and, thus, too large to induce standing-wave effects and concomitant spatial variations of the local DOS inside the linear CoCu$_n$Co chains whose lengths range from $\approx 1.3$ nm ($n = 2, m = 0$) to $\approx 2.3$ nm ($n = 4, m = 2$). Linear atomic clusters were previously used as resonators for electronic states [80–82], albeit at electron energies exceeding 1 eV. While these states exhibit Broglie wavelengths that match the dimensions of the linear clusters, their energies are too far from $E_F$ where the ASK resonance is located.

4. Conclusions

Non-local electron correlations between distant Kondo atoms can be influenced by their hybridization with non-magnetic atoms and probed by changes in the Abrikosov–Suhl–Kondo resonance line shape. The effect is sensitive to the hybridization geometry and corroborates that the anisotropic electronic structure at the Kondo impurity site is important for correlation effects. So far, state-of-the-art modelling has not been able to reproduce the presented experimental findings, which, therefore, call for honing of theoretical methods.

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ORCID iDs

N Néel https://orcid.org/0000-0003-0498-9138
J Kröger https://orcid.org/0000-0002-6452-5864
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