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Preserved Kondo effect of small cobalt atomic chains on Ru(0001) surface
Supplementary material for this article is available online.

Abstract

The evolution of the Kondo effect from a cobalt monomer to a compact dimer, a linear trimer and then a triangular trimer on Ru(0001) surface was studied by atomic manipulation and scanning tunneling spectroscopy (STS). It is found that the Kondo resonances of a compact Co dimer and linear trimer still can be detected in their STS because of the weak ferromagnetic exchange interaction between the Co atoms. However, when the number of the nearest-neighbors for every Co atom in the compact Co clusters is larger than two, for the interaction between Co atoms enter into the regime of the strong ferromagnetic exchange interaction, the Kondo resonance disappear and a new state forms.

Introduction

The interactions between localized electrons and delocalized electrons play a vital role in many cutting-edge fields of condensed matter physics. Kondo effect is one of the simplest examples. The Kondo effect occurs when the magnetic impurities are placed on the non-magnetic metal host, typically arises from the spin-flip scattering between the magnetic impurities and conduction electrons of the metal host, and results in a highly correlated ground state screening the magnetic moments of the impurities at temperatures below a characteristic Kondo temperature $T_K$. When the concentration of the magnetic impurities is increased or the distances between the magnetic impurities are reduced, the magnetic interactions between the magnetic impurities, including magnetic dipolar coupling, direct exchange between the impurities due to an overlap of the impurity d orbitals and the Ruderman–Kittel–Kasuya–Yosida (RKKY) interaction, become more and more important. All these interactions may modify the Kondo resonance considerably.

Earlier, the Kondo effect was studied in dilute magnetic alloys system. Later, with the development of the scanning tunneling microscope (STM), it has been widely extended to the adsorption system of the magnetic atoms and molecules. Using atomic manipulation and scanning tunneling spectroscopy, 3d magnetic transition metal atoms adsorbed on the 1B group surface, such as Au, Ag and Cu surfaces, have been extensively studied and well understood [2, 3]. A measurable Kondo effect was revealed as the magnetic impurities coupling with the conduction electrons of the Au [4, 5], Ag [6, 7], Cu [8–10], Rh [11], and Ru [12–14] surface. In the differential conductance spectrum, the Kondo effect manifests as a resonance residing upon the Fermi level which can be described by a Fano line shape [4, 15, 16]. The magnetic atoms coupled to different substrates show different magnetic ground states, thereby they display different Kondo resonances with different symmetries and different Kondo temperatures. When approached by other magnetic atoms, the Kondo resonance may be modified considerably for the assisting of the magnetic interactions between magnetic atoms [17–20]. The interaction between the Co atoms adsorbed on Cu(100) surface is RKKY interaction [20], because a correlated state with a new and lower Kondo temperature occurs due to the strong ferromagnetic exchange interaction between Co atoms, the Kondo resonance in the compact dimer disappears apparently. Our recent studies also observed the vanishing of the Kondo resonance for Co dimer constructed on Rh(111) surface [11]. As two Ni
atoms were pushed closer and closer on Au(111) surface, the orbital hybridization resulted in the splitting of the d orbital, and a new Kondo molecule Ni$_2$ with low Kondo temperature formed [19]. In addition, the magnetic chains can exhibit collective correlated states due to the interaction between magnetic atoms [20, 21]. But in our experiment, we found that the evolution of the Kondo effect from a cobalt monomer to a compact dimer, a linear trimer and then a triangular trimer on Ru(0001) surface is very different from the above situations.

Here we report a new phenomenon that the Kondo resonances of linear Co compact chains keep preserved on Ru(0001) surface. Using low-temperature STM, we found that the Kondo temperature of the isolated Co atom adsorbed on Ru(0001) surface is high for the strong interaction between Co atoms and Ru(0001) surface. Because the d orbitals of a single Co atom are more localized, the interaction between atoms becomes weaker, and the d orbitals are almost unaffected each other when the isolated Co atoms merge into a compact Co dimer then a linear trimer, their Kondo resonances remain as peaks and Kondo temperature is also unchanged. When the configuration of the compact trimer is changed from a line to a triangle, the interaction among the Co atoms is enhanced since the third Co atom is pushed closer to the Co dimer, resulting in a reduced Kondo temperature for the closer single Co atom and Co dimer. After the formation of the compact triangular trimer, when we continuously increase the number of atoms in the compact Co clusters, the Kondo resonance disappear apparently because of the formation of a new state above the Fermi level.

**Experimental section**

All the experiments were performed by using an Omicron low temperature STM installed in an ultrahigh vacuum chamber with a base pressure of $5 \times 10^{-11}$ mbar. The Ru(0001) sample was cleaned by cycles of Ar$^+$ sputtering (1000 eV) at room temperature and flash annealing to 1120 K. The Ru(0001) sample was then cooled to 5 K and dosed in UHV with a calibrated cobalt evaporator. In order to obtain a Ru(0001) sample with isolated single magnetic impurities adsorbed on it, the cobalt atoms were dosed in situ when the substrate was hold at about 10 K. All the measurements were performed with an electrochemically etched tungsten tip which was subjected to Ar$^+$ sputtering prior to all measurements. $dI/dV$ spectra were measured through lock-in detection of the ac tunnel current driven by a 731 Hz, 4 mV (rms) signal added to the junction bias. All the STM images in this work were recorded in a constant-current mode. When the Co atoms were manipulated on the surface, the tunneling condition was changed to 20 mV and 0.16 $\mu$A.

**Results and discussion**

By using the STM manipulation technique, the distant Co monomers were pushed to a clean area to form a compact Co dimer and then a linear trimer, the process is shown in figures 1(a)–(c). In order to show the intrinsic characteristics and differences of the Kondo resonances of the Co monomer, dimer and linear trimer better, their $dI/dV$ spectra, are displayed together in figure 1(d). In order to extract the resonance character and minimize the features originating from the tip or substrate electronic structures, we have subtracted a background spectrum acquired on the bare Ru(0001) surface with the same feedback conditions and the same tip from all the $dI/dV$ spectra shown in figure 1(d). It is obvious that the Kondo resonances remain near the Fermi level on the compact dimer and linear trimer as well as on the Co monomer. Apparently, they show some differences on the line shape and resonance position. But the essential properties should be extracted by fitting these Kondo resonances with Fano function with a linear background [4, 15, 22, 23] (see Fitting methods in the Supporting Information). By using atomic manipulation of STM, 10 different Co dimers were constructed with seven different tips, therefore there were 10 sets of the $dI/dV$ spectrum taken on Co dimers as well as monomers. Though it is difficult to construct a compact Co linear trimer, 4 different compact Co linear trimers were obtained, the $dI/dV$ spectra taken on the center of the linear trimer revealed no difference with that taken on the edges (not shown). Through the Fano fitting and statistical analysis, three main fitting parameters ($\varepsilon_0$, $\Gamma$ and $q$) of the compact dimer and linear trimer were obtained and shown in table 1 for contrast. It is strange that the width of the three different Kondo resonances almost remain a constant ($\sim$60 meV), which corresponds to a Kondo temperature $T_K \approx 350$ K. It is much higher than the previously reported Kondo temperature of the magnetic adatoms adsorbed on noble metal surfaces [4, 6, 7, 10, 24–32]. As shown in table 1, all the three fitting parameters of the Co dimer and linear trimer are almost the same, it can be easily deduced that a longer linear Kondo molecule will form as the Co chain becomes longer than two atoms, the chain can be considered as constituted by dimers in line. The main differences between the Co monomer and dimer lie in the resonance position and the line shape. The resonance position $\varepsilon_0$ of the Co dimer is about 5 meV below the Fermi level, however the Kondo resonance of the Co monomer is almost located at the Fermi level. And the absolute value of the line shape factor $q$ of the Co monomer ($\sim$31) is much larger than that of the Co dimer ($\sim$5), the Kondo resonance of the Co monomer is more symmetric than that of the Co dimer.
In order to understand the evolution of the Kondo effect from a cobalt monomer to a compact dimer, a linear trimer and then a triangular trimer on Ru(0001) surface, we firstly study the Kondo resonances of the cobalt monomer and pairs particularly.

It has been reported previously that \([4, 8]\), when the cobalt atoms adsorbed on the Au(111) and Cu(111) surface, their Kondo resonances all vanished at a distance of \(\sim 10\) Å from the center of the Co atom. But it is obviously different in our experiment. The spatial dependence of the Kondo resonance of a single Co atom was investigated by detecting the \(dI/dV\) spectra with a STM tip held at different distances from the center of the atom. As shown in figure 2, the Kondo resonance becomes weaker and weaker from the center to the edge of the Co atom, and vanishes at a distance of 6.9 Å from the center of the atom where the tip has left the Co atom. It seems that the Kondo effect in our experiment is more spatially localized than that on Au(111) and Cu(111) surface. According to the Fano function with a linear background \([4, 15, 22, 23]\), all the resonances were fitted and displayed by the circle dots, as shown in figure 2. Three main fitting parameters \((\varepsilon_0, \Gamma, q)\) were found to be almost the same for all those curves, and only the peak intensity changes. This is also different from the case of single Co atom on Au(111) surface \([4, 5]\), where the resonance line shape \((q < 1)\) tended to become more symmetric as the tip was moved outward, this means that the line shape factor \(q\) approached to 0 and the coupling between the STM tip and the continuum state became larger. But in our experiment, the resonance line shape \(q\) almost did not change when the tip was moved outward and vanished when the tip just left the hump shown in the inset of figure 2. That’s because Kondo resonance is mainly contributed by the tunneling between the tip and the local discrete state. Since the spatial dependence of the Kondo resonance reflects the spatial extent of the Co d orbitals, it means that the Co d orbitals is more spatially localized on Ru(0001) surface than on Au(111) and Cu(111) surface.

Table 1. The averages of the Kondo resonance position \(\varepsilon_0\), the full width at half maximum \(\Gamma\) and line shape factor \(q\) of a Fano resonance fitting to the \(dI/dV\) spectra of the cobalt monomers, dimers, and linear trimers on Ru(0001) measured at 5 K.

| Type         | \(\varepsilon_0\) (meV) | \(\Gamma\) (meV) | \(q\)   |
|--------------|-------------------------|------------------|--------|
| Monomer      | \(-0.4 \pm 1.0\)       | \(60.4 \pm 1.6\) | \(-31 \pm 8\) |
| Dimer        | \(-5.0 \pm 1.4\)       | \(60.0 \pm 1.8\) | \(-5 \pm 1\)  |
| Linear trimer| \(-5.1 \pm 1.1\)       | \(62.5 \pm 2.0\) | \(-5 \pm 1\)  |
Figure 2. A series of $dI/dV$ spectra taken with the STM tip held at various lateral positions from the center of an isolated Co monomer. ($V_s = 0.3 \, \text{V}, \, I_t = 6 \, \text{nA}$) Inset: the side view of a Co monomer. The constant $dI/dV$ curve of the Ru surface has been subtracted from each curve. The dotted curves show the fitting of a Fano function with a linear background to the data.

Figure 3. The initial $dI/dV$ spectra, structural models and topographic images (from bottom to top) for a pair of Co atoms with a separation of $3.3 \, \text{Å}, \, 4.2 \, \text{Å}, \, \text{and} \, 4.7 \, \text{Å}$ respectively. As a consistency check, spectra taken on both ends of the pairs are same. The bottom $dI/dV$ spectra for an isolated monomer and a compact dimer (2.7 Å) have subtracted a background spectrum acquired on the bare Ru(0001) surface with the same feedback conditions and the same tip, the circular dotted curves show the fit of a Fano function with a linear background to the data. All the black curves are measured above an isolated cobalt monomer at infinite distance (> 10 Å) for comparison.
It is also well known that, when the distance between two isolated Co atoms on surface become smaller and smaller, the coupling caused by the RKKY interaction between them will compete with the Kondo effect and affect the latter. With the formation of a compact Co dimer on Au(111) and Cu(100) [17, 20], the coupling between two Co atoms was a strong ferromagnetic exchange interaction, and the Kondo resonance disappeared because the Kondo temperature became much lower than the experimental temperature. However, in our experiment, the coupling between two Co atoms is so weak that the Kondo effect of the cobalt monomer is rarely affected by the other cobalt atom.

Figure 3 shows different cobalt pairs and dimer configurations with interatomic distances ranging from 4.7 to 2.7 Å together with the corresponding dI/dV spectra. We found that the spectrum taken on both ends of the Co pairs were the same (not shown). The Kondo resonances acquired on the Co pairs (shown by dark yellow lines in figure 3) are entirely the same with those acquired on the isolated Co monomer (shown by black lines in figure 3) until the interatomic distance reaches 3.3 Å, where the Kondo resonance of the Co pair become slightly different from that of the isolated Co monomer. After a compact Co dimer was constructed, the Kondo resonance did not disappear as previous work [17, 20], but only had some obvious changes in the intensity and resonance position. Both of the resonance can be well fitted with the Fano function, as shown in figure 3.

Although the Kondo effect preserve when the cobalt atoms are keep in line, the Kondo resonance can easily be affected when the configuration of the trimer was changed from a linear shape to a triangle and then disappear with the formation of a compact triangular trimer.

In the process of constructing the compact triangular trimer, we found that the width of Kondo resonances on both of the Co monomer and compact dimer became narrower obviously as the Co monomer were pushed closer to a compact dimer laterally, as shown in figure 4(a). The widths of the three different Kondo resonances

| Figure 4. (a) The Kondo resonances of a Co monomer (marked with ‘1’) and Co dimer (marked with ‘2’) in close proximity, the Kondo resonance of isolated monomer was shown for comparison. (b) The initial dI/dV curves obtained on the bare Ru(0001) surface, a cobalt monomer and a compact triangular trimer. The insets show the STM images and the corresponding structure models. |
were obtained by fitting their spectra with a Fano function, they were 52.1 meV, 50.3 meV and 60.2 meV for the closer monomer, closer compact dimer and isolated monomer respectively. Since it is very difficult to precisely control the distance of the closer monomer and compact dimer, the evolvement of their Kondo resonance with the distance and configuration is hard to study carefully.

As the closer monomer was pushed to the compact dimer and a compact triangular trimer formed at last, the Kondo resonance vanished, as shown in figure 4(b). The disappearance of Kondo resonance was further confirmed by checking 10 sets of dI/dV spectrum on 10 different compact triangular trimers (not shown), all the dI/dV spectra of the compact triangle trimers nearly exhibit the same character with that of the bare Ru surface, as shown in figure 4(b).

From the above results, it can be seen that the Kondo resonance of the Co cluster is significantly affected by the numbers of the nearest-neighbors of Co atoms. By using atomic manipulation, the number of Co atoms in the compact clusters can be increased from 1 to 6, the process was shown in figure S2 in the supporting information. The dI/dV spectra of the compact Co clusters with different number of Co atoms (n = 1–6) are shown in figure 5. Comparing these spectra of Co clusters with that of the bare Ru surface, new states marked with black dashed line appear indeed despite the change of the tip, the gray dashed line mark the special tip states of this two tips.

The Kondo effect of the Co atoms or clusters on Ru(0001) surface can be understood in qualitative as below. It is obvious that the spin of the d orbitals of the Co monomer on Ru(0001) surface is not degenerated, as the conduction band electrons of the Ru(0001) surface interact with the unpaired electrons of Co monomer, the
Kondo resonance emerges due to the spin flip scattering at the low temperature. The most complicated phenomenon is that the Kondo resonance persist on compact Co dimer and linear trimers and their Kondo temperature almost remain a constant, which is significantly different from the case on Au(111) and Cu(100) surface [17, 20], where the ferromagnetic interaction between the cobalt atoms become very strong and the Kondo resonances of the compact dimers disappear. For the magnetic impurities in these three systems are all cobalt atoms, the difference among the three systems should come from the different substrates. It is instinctive that the coupling between the Co atoms and Ru(0001) surface is much stronger than that in the other two systems, and we also found that the d orbital of Co monomer is more localized on Ru(0001) than on Au(111) and Cu(100), so it is reasonable that the ferromagnetic interaction between the Co atoms in the compact Co dimer and linear trimer is much weaker than the case on Au(111) and Cu(100) surface [17, 20], and maintain in the intermediate exchange interaction regime [20, 33], the single-impurity Kondo resonance operates, and the Kondo resonance of compact Co dimer and linear trimers almost maintains the characteristics of Co monomer. As the number of the nearest-neighbors for every Co atom in the clusters increased to above two, the interaction between the Co atoms become much stronger, and a new state forms in the d\(I/dV\) spectra in figure 5. One of reason may be similar with the disappearance of the Kondo resonance of the compact Co dimer on Au(111) and Cu(100) [17, 20], when the coupling among these Co atoms in compact triangular trimer become a strong ferromagnetic exchange interaction \(J_{\text{Co-Co}} \gg T_K\) monomer, the Kondo temperature \(T_K\) trimer \(= (T_K)\) monomer \(\propto r^3\) Co-Co [34], so the Kondo temperature becomes much lower than the experimental temperature. Because the Kondo resonances can not be detected in these large clusters, another reason can not be excluded, it is that the Kondo effect may be suppressed completely by the strong ferromagnetic exchange interaction.

### Conclusion

In summary, we find that the Co monomer adsorbed on Ru(0001) surface shows high Kondo temperature because of the strong coupling between the Co atoms and substrate. Due to the more localized d orbitals of Co atoms on Ru(0001) surface and weaker interaction between the Co atoms, the ferromagnetic interaction between the Co atoms in the compact Co dimer and linear trimer enters into an intermediate exchange interaction regime, the Kondo resonance of a compact Co dimer and linear trimer nearly maintain the characteristics of Co monomer, that is the Kondo resonances remain peaks and Kondo temperature almost remains a constant. As the configuration of the trimer was converted from a line to a triangle, the Kondo temperature becomes much lower than the experimental temperature. Because the Kondo resonances can not be detected in these large clusters, another reason can not be excluded, it is that the Kondo effect may be suppressed completely by the strong ferromagnetic exchange interaction.

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### References

[1] Hewson A C 1993 *The Kondo Problem to Heavy Fermions* (Cambridge: Cambridge University Press)
[2] Brune H and Gambardella P 2009 Science **603** 1812–30
[3] Ternes M, Heinrich A J and Schneider W D 2009 *J. Phys.: Condens. Matter* **21** 053001
[4] Madhavan V, Chen W, Jamneala T, Crommie M F and Wingreen N S 1998 *Science* **280** 567–9
[5] Madhavan V, Chen W, Jamneala T, Crommie M F and Wingreen N S 2001 *Phys. Rev. B* **64** 165412
[6] Schneider M A, Vitali L, Knorr N and Kern K 2002 *Phys. Rev. B* **65** 121406
[7] Wahl P, Diekhoner L, Schneider M A, Vitali L, Wittich G and Kern K 2004 *Phys. Rev. Lett.*** 93** 176603
[8] Manoharan H C, Lutz C P and Eigler D M 2000 *Nature* **403** 512–5
[9] Prüser H, Wendoroth M, Dargel P E, Weismann A, Peters R, Pruschke T and Ulbrich R G 2011 *Nat. Phys.* **7** 203–6
[10] Knorr N, Schneider M A, Diekhoner L, Wahl P and Kern K 2002 *Phys. Rev. Lett.* **88** 096804
[11] Feng W and Zhao A 2012 *Acta Phys. Sin.* **61** 173601
[12] Ren J, Guo H, Pan J, Zhang Y Y, Wu X, Luo H G, Du S, Pantleides S T and Gao H J 2014 *Nano Lett.* **14** 4011–5
[13] Ren J, Wu X, Guo H, Pan J, Du S, Luo H G and Gao H J 2013 *Appl. Phys. Lett.* **103** 071604
[14] Feng W, Liu Q, Liu X and Zhao A 2016 *Nanotechnology* **27** 455203
[15] Fano U 1961 *Phys. Rev.* **124** 1866
[16] Ujágyi O, Kroha J, Szunyogh L and Zawadowski A 2000 *Phys. Rev. Lett.* **85** 2557–60
[17] Chen W, Jamneala T, Madhavan V and Crommie M F 1999 *Phys. Rev. B* **60** R8829
[18] Jamneala T, Madhavan V and Crommie M F 2001 *Phys. Rev. Lett.* **87** 256804
[19] Madhavan V, Jamneala T, Nagaoka K, Chen W, Li J L, Louie S G and Crommie M F 2002 *Phys. Rev. B* **66** 212411
[20] Wahl P, Simon P, Diekhöner L, Stepanyuk V S,.blur P, Schneider M A and Kern K 2007 *Phys. Rev. Lett.* **98** 056601
[21] Hirjibehedin C F, Lutz C P and Heinrich A J 2006 *Science* **312** 1021–4
[22] Wahl P, Diekhöner L, Schneider M A and Kern K 2010 Rev. Sci. Instrum. 79 043104
[23] Bork J, Zhang Y-H, Diekhöner L, Borda L, Simon P, Kroha J, PeterWahl and Kern K 2011 Nat. Phys. 7 901–6
[24] Otte A F, Ternes M, von Bergmann K, Loth S, Brune H, Lutz C P, Hirjibehedin C F and Heinrich A J 2008 Nat. Phys. 4 847
[25] Jamneala T, Madhavan V, Chen W and Crommie M F 2000 Phys. Rev. B 61 9990
[26] Nagaoka K, Jamneala T, Grobis M and Crommie M F 2002 Phys. Rev. Lett. 88 077205
[27] Li J T, Schneider W D, Berndt R and Delley B 1998 Phys. Rev. Lett. 80 2893
[28] Heersche H B, de Groot Z, Folk J A, Kouwenhoven L P, van der Zant H S J, Houck A A, Labaziewicz J and Chuang I L 2006 Phys. Rev. Lett. 96 017205
[29] Vitali L, Ohmann R, Stepanow S, Gambardella P, Tao K, Huang R, Stepanyuk V S, Bruno P and Kern K 2008 Phys. Rev. Lett. 101 216802
[30] Otte A F, Ternes M, Loth S, Lutz C P, Hirjibehedin C F and Heinrich A J 2009 Phys. Rev. Lett. 103 107203
[31] Kawahara S I, Lagoute J, Repain V, Chacon C, Girard Y, Klein J and Rousset S 2010 Phys. Rev. B 82 020406
[32] Neel N, Kroger J and Berndt R 2010 Phys. Rev. B 82 233401
[33] Jayaprakash C, Krishna-murthy H R and Wilkins J W 1981 Phys. Rev. Lett. 47 737
[34] Savkin V V, Rubtsov A N, Katsnelson M I and Lichtenstein A I 2005 Phys. Rev. Lett. 94 026402