The Kondo tip decorated by the Co atom

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The Kondo tip decorated by the Co atom

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Abstract
The Kondo effect of single Co adatoms on Ru(0001) is detected with two different kinds of co-decorated tip (Kondo tip) by using low temperature scanning tunneling microscopy and scanning tunneling spectroscopy. We call the relatively separated two magnetic impurities in the tunneling region ‘two Kondo system’ to distinguish it from the ‘two-impurity Kondo system’. We find that the artificially constructed Kondo tips can be generally categorized into two types of Kondo resonances, which have distinct Fano line shapes with quantum interference factor \(|q|/1 \gg 1|q|/1 \sim 1\), respectively. The tunneling spectra of six constructed two Kondo systems can be well fitted by summing the two Fano resonances of the two subsystems and a linear background. More interestingly, by extracting the amplitudes of the two Fano resonances in the spectra, we find that the electron transmission of such a two Kondo system in the tunneling region is dominated by the quantum interference of the Kondo tip, which is directly related to the geometric configuration of the adsorbed Kondo atom on the tip.

Keywords: Kondo effect, STM, cobalt atom, Ru(0001), two-impurity Kondo system

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

1. Introduction

The Kondo effect is an interesting physical phenomenon in condensed matter physics, which has been extensively studied on single-atom level by scanning tunneling microscopy (STM) [1, 2]. When single magnetic impurities adsorb on a non-magnetic metal surface, the conduction electrons of the substrate are scattered by the magnetic moment of the magnetic impurities. Below a characteristic temperature \(T_K\), a single non-magnetic ground state forms and the spin of the magnetic impurity is completely screened by the conduction electrons as a result of the Kondo effect [3]. In the \(dI/dV\) spectra detected on single magnetic impurities, the non-magnetic ground state leads to a Kondo resonance on Fermi level, which can be fitted by a single Fano line shape [4–12]. Because the \(dI/dV\) spectrum is proportional to the convolution of the density of states of the tip and sample [13], if we want to get the quantitative characteristic of the Kondo resonance, it is necessary to exclude the interference of the density of states of the tip. According to the literature, there are three main methods to obtain the quantitative characteristic of the Kondo resonance by processing the \(dI/dV\) spectra. The first method is considering the density of states of tip as a constant and fitting the \(dI/dV\) spectrum directly by a Fano line shape [5, 7, 9, 14–16]. The second method is subtracting the \(dI/dV\) spectrum of the substrate surface as a background from the \(dI/dV\) spectrum of the magnetic impurity and then fitting the subtracted \(dI/dV\) spectrum by a Fano line shape [17, 18]. The third method is performing background subtraction by deconvoluting the spectrum detected on the magnetic impurity with the spectrum detected on the substrate with the same tip [18]. However, in our experiments, when single Co atoms are attached to the tips, we find that the Kondo resonance of the Co adatoms on Ru(0001) detected with these different special tips can not be correctly described by the above three conventional methods. Appropriate fitting results can be obtained only when considering the special tip and surface adatoms as two independent Kondo systems respectively and then adding them proportionally [19, 20]. Therefore, when the Kondo resonance of the magnetic impurities adsorbed on substrate surface are studied by STM, it is important to ensure that...
there are not any magnetic impurities adsorbed on the tip, otherwise a precise quantitative understanding of the Kondo resonance cannot be obtained.

When two magnetic impurities come close to each other on atomic level, they constitute a two-impurity Kondo system, which in particular refer to the situation that there are complicated interactions between the two magnetic impurities because of the competition between the Kondo screening and magnetic interaction. When the two magnetic impurities are separated in the tunneling region, we call them two Kondo systems to distinguish it from the two-impurity Kondo system. Therefore previous studies of two-impurity Kondo system are mainly performed by theoretical methods [21–29] because it is difficult to fabricate a two-impurity Kondo system by most of the experimental techniques. Yet, the two-impurity Kondo system can be implemented by using STM [15, 19, 30] and lithographic technology [31–33]. Once the distance between the two impurities can be controlled accurately on atomic level, the development of the Kondo resonance in a two-impurity Kondo system can be understood in details. Kern’s group firstly realized the precise control of the distance between two Kondo impurities, and obtained a phase diagram of the two-impurity Kondo system [20]. In tunneling spectra, the Kondo resonance is detected as a Fano line shape due to interference between electrons tunneling into the conduction band of the substrate and electron tunneling into the Kondo state. Depending on the relative strengths of the two channels, the line shape of the Kondo resonance can be a dip ($q | \approx 0$), an asymmetric line shape ($q | \approx 1$) or a peak ($q | \gg 1$). In previous work [20, 34], the Kondo resonances of the tip and substrate system are all the similar shape (both of them exhibit an asymmetric line shape ($q | \approx 1$) or a peak line shape ($q | \gg 1$)). Until now, the understanding of the tunneling spectra of the different kinds of two Kondo system in the tunneling region as well as the location of Co atoms adsorbed on STM tip is not sufficient. In our experiments, we construct two kinds of tip Kondo system by picking up a Co atom from the Ru(0001) surface, one shows a Kondo resonance with a peak line shape ($q | \gg 1$) and the other displays a Kondo resonance with an asymmetric line shape ($q | \approx 1$). Then we respectively analyze the two kinds of two Kondo system in the tunneling region, one of the subsystem is this two kinds of tip Kondo system, the other is the substrate Kondo system which is single Co atom adsorbed on Ru(0001) surface. We find that new resonances form near the Fermi level in these two Kondo systems. When considering the weight of each Kondo system in the superposition, the new resonances are mainly affected by the tip Kondo system.

2. Experiments and methods

All the experiments were performed in an ultra-high vacuum chamber installed with a low temperature STM (Omicron GmbH) with a base pressure of $3 \times 10^{-11}$ mbar. The Ru(0001) sample was cleaned by cycles of Ar$^+$ sputtering (1000 eV) at room temperature and flash annealing to 1120 K. The clean Ru(0001) sample was then cooled to 5 K, and cobalt atoms (Co rod, purity 99.99% from Mateck) were deposited in situ by using calibrated e-beam evaporator source (Omicron EFM-3T), the temperature of the sample was kept below 10 K during the evaporation process. An electrochemically etched clean tungsten tip was used in our experiment. The $dI/dV$ spectra were measured through the lock-in detection (Stanford Research SR830) of tunneling current modulated by a 731 Hz, 4 mV (rms) signal added to the junction bias. All the measurements were performed at 5 K, and all the STM images were recorded in a constant-current mode.

3. Results and discussion

First, we prepared a substrate Kondo system by in situ deposition of Co atoms on Ru(0001) substrate. Figure 1(a)
Table 1. The single Fano fitting parameters and the sum of two Fano fitting of the Kondo resonances detected with Kondo tip I₁ and II₁ in figure 4.

<table>
<thead>
<tr>
<th></th>
<th>ε₀ (mV)</th>
<th>Γ/2 (mV)</th>
<th>q</th>
<th>a₁</th>
<th>a₂</th>
<th>a₁/a₂</th>
<th>Amplitude ratio $F_{\text{max}}(a_{1f\text{Co@tip}(\varepsilon)})/F_{\text{max}}(a_{2f\text{Co@sub}(\varepsilon)})$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Clean tip</td>
<td>On Co</td>
<td>−0.4</td>
<td>30.0</td>
<td>−31</td>
<td>0</td>
<td>1</td>
<td>—</td>
</tr>
<tr>
<td>Kondo tip I₁</td>
<td>On Ru</td>
<td>0.5</td>
<td>10.5</td>
<td>−8.0</td>
<td>1</td>
<td>0</td>
<td>— 5.93</td>
</tr>
<tr>
<td></td>
<td>On Co</td>
<td>0.3</td>
<td>11.5</td>
<td>−30</td>
<td>0.02288</td>
<td>0.00023</td>
<td>99</td>
</tr>
<tr>
<td>Kondo tip II₁</td>
<td>On Ru</td>
<td>−3.2</td>
<td>8.0</td>
<td>0.58</td>
<td>1</td>
<td>0</td>
<td>— 0.42</td>
</tr>
<tr>
<td></td>
<td>On Co</td>
<td>2.3</td>
<td>25.0</td>
<td>−16</td>
<td>0.01463</td>
<td>0.00007</td>
<td>209</td>
</tr>
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shows the STM image of individual Co atoms adsorbed on Ru(0001) surface. The protrusions with identical height are the isolated single Co adatoms. The typical $dI/dV$ spectra acquired on the Ru substrate and the single Co atoms are shown in figure 1(b). The $dI/dV$ spectrum obtained on the Ru substrate (gray solid line) with a clean tip is featureless, while there is a sharp peak just located at the Fermi energy in the $dI/dV$ spectrum of the Co adatom (red solid line). This peak is just caused by the Kondo resonance \[ \varepsilon = \frac{-\varepsilon_0}{\Gamma/2} \] In order to fit the experiment data best, a constant and a linear background term can be taken into account \[ g(\varepsilon) = a\varepsilon + b\varepsilon + c. \] Thus three main parameters of the Kondo resonance, including the position $\varepsilon_0$, half width $\Gamma/2$ of the resonance and a line-shape parameter $q$, can be extracted from the fitting. By using equation (2), we can fit the experimental data very well, as shown by the orange dashed line in figure 1(b). Measurements conducted on ten different single Co adatoms with ten different clean tips yield the average value $\varepsilon_0 = -0.4 \pm 1$ meV, $\Gamma/2 = 30.2 \pm 0.7$ meV, and $q = -31 \pm 8$. These parameters are listed in table 1. The Kondo temperature $T_K$ of single Co adatoms on Ru(0001) surface is about 350 K, larger than that on other surfaces [5, 7, 9, 16, 17, 19].
The above paragraph describes one subsystem of the two Kondo system, i.e. the substrate Kondo system. Then we construct the other subsystem, i.e. the tip Kondo system, by picking up a Co adatom from Ru(0001) surface with a clean tip. The specific process is shown in figure 2. First, we chose a Co adatom (indicated by the white arrow in figure 2(a)) on the Ru(0001) surface, which can be identified by its characteristic Kondo resonance. Then we picked up this single Co atom by STM tip through positioning the tip on top of this adatom and applying a +2.0 V sample bias pulse [20, 36] (figure 2(b)). Once the picking-up procedure succeeds, the Co atom disappears on the surface (see figure 2(c)). In our experiment, there is one type of tip, which can reversibly transfer the Co atom back to the Ru surface from tip-apex (see figure 2(e)) by applying small negative voltage pulse. The schematic of this procedure is shown in figure 2(d). This type of tip with an attached Co atom exhibits a very sharp Kondo peak (lql ≫ 1) and is denoted as Kondo tip I in this work. This type of Kondo tip can repeatedly drop off and pick up a single Co atom under the same conditions, and the Kondo resonance completely remains unchanged when the tip picks up a different single Co atom, as shown in figure 3. The other type of tip attached by Co atoms exhibit an asymmetric line shape Kondo resonance (lql ~ 1) and the attached Co atom cannot be dropped off to the Ru surface. We denote them as Kondo tip II.

Figure 4 shows the dI/dV spectra obtained on the substrate (red solid line) and above a single Co adatom (blue solid line) with two typical Kondo tip I₁ and II₁. In contrast, the dI/dV spectra of the Ru surface (gray solid line) detected by the clean tip before picking up a single Co adatom are featureless. Using the formula (2), we fitted the Kondo resonances of the corresponding Kondo tips, the parameters are listed in table 1. The Kondo resonance of Kondo tip I₁ appears as a peak, corresponding to the fitting parameters ε₀ = 0.5 meV, Γ/2 = 10.5 meV and q = −8. The fitting parameters for Kondo tip II₁ are ε₀ = −3.2 meV, Γ/2 = 8.0 meV and q = 0.58, corresponding to an asymmetric line shape. According to recent work by Kern’s group [20], the Kondo resonance of two Kondo system in the tunneling region is the sum of the Kondo resonances of the tip Kondo system and the substrate Kondo system. The summation effect can be seen directly on the dI/dV spectra obtained on the single Co adatom with Kondo tip II₁, as shown in figure 4(b). It is obvious that the first method mentioned in introduction is not suitable for fitting these two types of Kondo resonance directly, especially for Kondo tip II₁. Also, if the Kondo resonance of the substrate Kondo system is extracted by using the second method mentioned in
introduction (subtracting the $dI/dV$ spectra of the Ru substrate as a background from the $dI/dV$ spectra of the Co adatom obtained with the same clean tip), then they are fitted with a single Fano line shape, the fitting parameters are listed in table 1, we can see that the extracted half-width $\Gamma/2$ of the Kondo resonance is narrower than that measured on Co adatoms by clean tip, and the line-shape parameter $q$ is also smaller. The third method mentioned in the introduction has also been used to fit the two types of Kondo resonance, but we find that the fitting results are not convergent. So this will engender a misconception of the Kondo effect of the magnetic impurity adsorbed on surface when the STM tip becomes a Kondo tip.

According to a sum of two Fano line shapes proposed by Kern group [20], the $dI/dV$ spectra obtained on the Co adatoms with Kondo tips can be fitted very well. The fitting function is as follows

$$g(\varepsilon) = a_1f_{\text{Co@tip}}(\varepsilon) + a_2f_{\text{Co@sub}}(\varepsilon) + b\varepsilon + c.$$  

In which the functions $f_{\text{Co@tip}}$ and $f_{\text{Co@sub}}$ express the tip Kondo system and substrate Kondo system with single Fano line shape, respectively; and the parameters $a_1$ and $a_2$ are their corresponding proportion. Here, a constant and a linear background are also considered [19, 20].

According to formula (3), the Kondo effect of single Co adatoms adsorbed on the Ru surface can be treated as the case of $a_1 = 0$ and $a_2 = 1$, while the Kondo effect of the Co atoms adsorbed on the tip can be treated as the case of $a_1 = 1$ and $a_2 = 0$, as shown in table 1. When we use the formula (3) to fit the $dI/dV$ spectra of the single Co adatoms measured by Kondo tip I$_1$ and II$_1$, the parameters used in $f_{\text{Co@tip}}$ (including $\varepsilon_0$, $\Gamma/2$ and $q$) are fixed and we adopt the single Fano fitting parameters of the corresponding Kondo tip on Ru in table 1. In the term of $f_{\text{Co@sub}}$, we use the single Fano fitting parameters of the clean tip on Co in table 1. The fitting curves are the green dashed lines in figures 4(a) and (b), they agree well with the experimental data. And the corresponding term $a_1f_{\text{Co@tip}}$ and $a_2f_{\text{Co@sub}}$ are also shown in the bottom. The corresponding parameters $a_1$ and $a_2$ are listed in table 1, it is obvious that the $dI/dV$ spectrum of the two Kondo system in tunneling region is mainly contributed by the Kondo

Figure 5. The $dI/dV$ curves obtained with other four different Kondo tips I$_2$, I$_3$, II$_2$, and II$_3$. All the dotted lines are the single Fano fitting of the different experimental curves.
Table 2. The single Fano fitting parameters and the sum of two Fano fitting of the Kondo resonances detected with clean tip, Kondo tip I₂, I₃, II₂, and II₃.

<table>
<thead>
<tr>
<th></th>
<th>Single Fano fit parameter $f(\varepsilon_0, \Gamma, q)$</th>
<th>Sum of two Fano fit $a_{1f_{Co@tip}(\varepsilon)} + a_{2f_{Co@sub}(\varepsilon)}$</th>
<th>Amplitude ratio $F_{\text{max}}(a_{1f_{Co@tip}(\varepsilon)})/F_{\text{max}}(a_{2f_{Co@sub}(\varepsilon)})$</th>
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<tbody>
<tr>
<td>Clean tip</td>
<td>$\varepsilon_0$ (meV) 30.0 $\Gamma/2$ (meV) 31 $q$ 0 1 $a_1/a_2$ —</td>
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<td></td>
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<tr>
<td>Kondo tip I₂</td>
<td>On Co $-0.4$ 24.0 $-16$ 1 0 $—$</td>
<td></td>
<td></td>
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<tr>
<td>Kondo tip I₃</td>
<td>On Co $-3.0$ 22.7 $-26$ 0.00072 0.00008 9</td>
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<td></td>
</tr>
<tr>
<td>Kondo tip II₂</td>
<td>On Ru $-3.2$ 11.3 $-16$ 1 0 $—$</td>
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<tr>
<td>Kondo tip II₃</td>
<td>On Co $0.8$ 17.0 $-28$ 0.00653 0.00081 8</td>
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resonance of the tip, because the value of $a_1$ is much larger than that of $a_2$.

To further verify this point, we also constructed other four different Kondo tips, based on the value of line shape parameter $q$, they are labeled as Kondo tip I$_2$, I$_3$ ($|q| > 1$) and I$_2$, I$_3$ ($|q| \sim 1$). The $dI/dV$ spectra obtained on Ru surface and single Co adatoms with these tips and the corresponding fitting curves are all shown in figure 5, and the fitting parameters are listed in table 2. Based on the single Fano fitting parameters of the Kondo tip on Co in table 2, we find that the position $\varepsilon_0$, half-width $\Gamma/2$ and line-shape parameter $q$ are quite different from the parameters obtained by single Fano fitting of single Co adatoms obtained with clean tip. Especially, the half-width $\Gamma/2$ are all smaller. Therefore, when studying the Kondo effect of the magnetic impurity adsorbed on surface by STM, one should ensure that the $dI/dV$ spectra obtained on the substrate is featureless and exhibit no Kondo resonance at the Fermi energy, otherwise the understanding of the Kondo effect is unconvincing. If we use the formula (3) to fit these $dI/dV$ spectra in figure 5, we also find that $a_1$ are always much larger than $a_2$, regardless of the width and line shape of the Kondo resonance in the tip Kondo system, it further proves that the $dI/dV$ spectra of the two Kondo system in tunneling region is mainly contributed by the Kondo resonance of the tip Kondo system.

Because the Kondo tip I can pick up and drop off single Co atoms repeatedly, we speculate that the adsorption site of the Co atom is just on tip-apex, the schematic diagram is shown in figure 6(a). When the attached single Co atom becomes the new apex atom of tip, the tunneling probability between the substrate electrode and the discrete states of the attached Co atom must be much greater than that between the substrate electrode and the continuous states of conduction electrons of the tip. According to the physical meaning of the line shape parameter $q$ [5, 6], this type of adsorption of the Co atom in figure 6(a) would make the value of $|q|$ greater than 1. In our experiment, the value of $|q|$ for three different Kondo tip I are indeed coincident with our speculation above (see tables 1 and 2). Because the attached Co atom on the Kondo tip II cannot be dropped off to the surface, we speculate that the adsorbed location of the Co atom is on the side of the tip, the schematic diagram is shown in figure 6(b). Because the neighboring atoms of attached Co atom in Kondo tip II are more than that in Kondo tip I, it is more difficult to transfer the attached Co atom back to the substrate for Kondo tip II. Because the attached Co atom is not on the tip-apex, the tunneling probability between the substrate electrode and the discrete state of the attached Co atom must be much smaller than that in Kondo tip I, leading to a smaller line shape parameter $|q|$. The value of $|q|$ for three different Kondo tip II in our experiment are indeed smaller, close to 1. Therefore, the proposed models in figure 6 are credible. The tip Kondo system used in Kern’s experiment [20] may correspond to the Kondo tip II in our work, where the attached Co atom maintain on the tip after the tip were approached to contact the cobalt atom on the substrate. But when we try to approach the Kondo tip I to the Ru surface or single Co adatom, the Co atom attached on Kondo tip I always drops off before atomic point contact occurs.

4. Conclusion

In conclusion, we have constructed two kinds of Kondo tip (I and II) after picking up single Co adatoms by clean STM tips, one with a Co atom attached just below the apex exhibits an obvious Kondo peak ($|q| > 1$), and the other with a Co atom attached on one side of the tip exhibits an asymmetric Kondo dip ($|q| \sim 1$). Each of them together with the substrate Kondo system (single Co atoms on Ru(0001) surface) form two different two Kondo systems. We find the $dI/dV$ spectrum of both two Kondo systems in tunneling region is the sum of the Kondo resonance of the substrate Kondo system and tip Kondo system, but mainly contributed by the Kondo resonance of the tip Kondo system. The method, extracting the Kondo resonance by subtracting the $dI/dV$ spectra of the substrate surface as a background from the $dI/dV$ spectra of
the magnetic impurity, is only feasible for clean tips with no magnetic impurity on it. Our findings have important significance for studying the Kondo resonance of the magnetic impurity adsorbed on surface by STM.

Acknowledgments

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