Spin-Resolved Splitting of Kondo Resonances in the Presence of RKKY-Type Coupling

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We have performed spin-resolved measurements on a Kondo impurity in the presence of RKKY-type exchange coupling. By placing manganese phthalocyanine (MnPc) molecules on Fe-supported Pb islands, a Kondo system is devised which is exchange coupled to a magnetic substrate via conduction electrons in Pb, inducing spin splitting of the Kondo resonance. The spin-polarized nature of the split Kondo resonance and a spin filter effect induced by spin-flip inelastic electron tunneling are revealed by spin-polarized scanning tunneling microscopy and spectroscopy.

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The Kondo effect originates from the screening of a local spin moment by the itinerant electron spins of a metallic host [1]. Below a characteristic temperature known as the Kondo temperature, a new many-body state named the Kondo resonance appears at the Fermi level which can be detected as a Fano resonance in scanning tunneling spectroscopy (STS) near the local spin [2,3]. On the other hand, RKKY coupling is responsible for magnetism in dilute magnetic systems, where individual localized magnetic moments indirectly couple to each other via conduction electrons as a medium. The competition between the Kondo effect and magnetic couplings removes the degeneracy of the spin state of the local moment and induces a spin splitting of the Kondo resonance. Therefore the Kondo effect has been utilized as a sensitive tool not only for single spin detection but also for characterization of magnetic interactions [4–8].

However, to date, investigations on Kondo physics of single spin states have only been performed with spin-averaged STS techniques, presumably due to the lack of appropriate systems which not only remove the degeneracy of Kondo resonances but also provide a magnetic anisotropy to favor a specific spin orientation [9]. In this regard, we show that by placing an otherwise degenerate Kondo system in proximity with a magnetic substrate, the spin degeneracy of the Kondo resonance is effectively removed due to the large exchange interactions mediated through conduction electrons, inducing the splitting of the Kondo resonance into two peaks. In addition, the blocked magnetization of a magnetic substrate provides a favored magnetization direction to the split Kondo resonances. We have demonstrated the spin-polarized nature of split Kondo resonances as well as a spin filter effect caused by inelastic spin-flip electron tunneling with spin-polarized scanning tunneling microscopy (STM) and STS, which has shown its success for studying magnetism down to single spin level [10–12].

The magnetic substrate consists of Fe stripes which are prepared by deposition of 8–10 atomic layers (AL) Fe on a W(110) substrate at room temperature followed by annealing at 1000 K for 15 min. The Kondo system is MnPc on Pb(111), which has been well characterized previously [13]. Pb with a nominal coverage of 1.5 AL and a submonolayer of MnPc were sequentially deposited onto the W-supported Fe surface at an estimated temperature of 70 K. Bare W tips and Fe-coated W tips were used for spin-averaged and spin-polarized measurements, respectively. The magnetic tip was prepared by coating the flashed W tip (to 2000 K) with 10 AL of Fe followed by annealing to 500 K for 10 min. The measurements were performed at 6 K with a homemade low temperature STM system [14]. All spectra were obtained by standard lock-in techniques with a modulation voltage of 1 meV at 1777 Hz.

The topography of Pb grown on W-supported Fe stripes is shown in Fig. 1(a), where Pb islands decorate the whole surface. On top of the Pb islands, monolayer MnPc molecules can be faintly seen. The Fe stripes are (110) surface oriented with an average height of 10 nm and a width of $\sim$300 nm, whose electronic properties can thus be considered as bulklike. As is schematically shown in Fig. 1(b), the W surface was first wet with 1 AL of Fe before the formation of Fe stripes. Similarly, on top of the Fe-pregrown surface, Pb islands with (111) orientation formed after covering the whole surface with 1 AL of Pb known as the wetting layer. We notice that almost all Pb islands are 2 AL thick above the wetting layer, as a result of the quantum size effect on their growth behavior [15]. Pb atoms stack along the [001] direction of the underlying Fe(110) surface and keep the lattice constant of the Pb(111) surface, forming a moiré pattern of about $c(2 \times 5)$ [Fig. 1(d)] superimposed on both the wetting layer and the Pb island [Fig. 1(c)]. This is a hint for the absence of intermixing between the two atomic species [16], which ensures that the exchange interaction between MnPc and the Fe substrate is purely mediated through metallic Pb overlayers. MnPc molecules preferentially adsorb onto Pb islands and self-organize into ordered molecular lattices [Fig. 1(c)]. Single MnPc molecules can

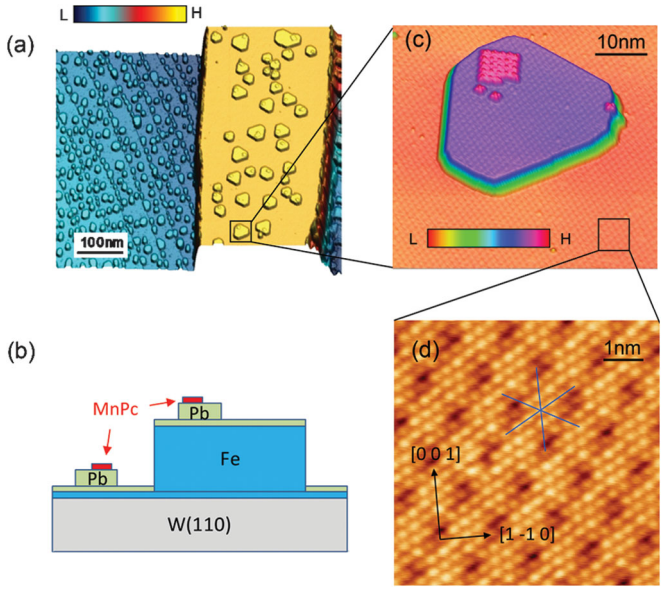

FIG. 1 (color). Morphology of the sample surface. (a) An overview STM image ($V = -5.0$ V, $I = 30$ pA) showing a W(110)-supported Fe nanostripe decorated with Pb islands, which is schematically illustrated in (b). (c) A pseudo-3D image ($V = -0.5$ V, $I = 0.1$ nA), which is zoomed in from (a), shows a Pb island on a Fe stripe with deposited MnPc molecules. (d) Atomic resolution of the Pb wetting layer, in which crystallographic directions of Fe(110) (black arrows) and Pb(111) (blue lines) are marked.

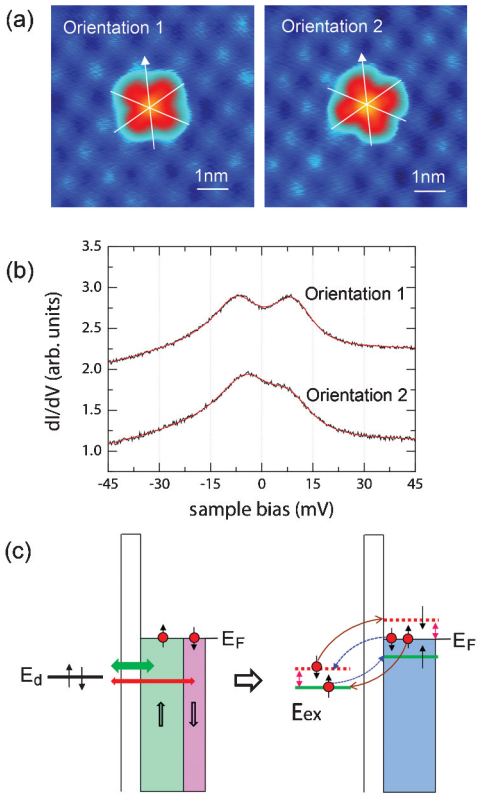

FIG. 2 (color). Spin-averaged STS of MnPc. (a) STM image ($V = -100$ mV, $I = 0.1$ nA) of MnPc with two different orientations. Crystallographic directions of Pb(111) (white lines) and Fe[001] direction (white arrow) are marked. (b) Typical tunneling spectra of MnPc with different orientations showing split Kondo resonances measured with a bare W tip (black curves) (tunneling gap: $V = -100$ mV, $I = 0.5$ nA). They have been offset for clarity. Red curves are the fitting curves with two Fano resonances. (c) Simplified schematics showing the physical principle of exchange coupling induced spin splitting of Kondo resonances. The green (red) box represents the majority spin-up (minority spin-down) band of the magnetic substrate. The spin-dependent interaction (represented with green and red left-right arrows of different boldness) with a localized spin splits its otherwise degenerate unpaired orbital (E_d), where the solid green (dashed red) line marks its ground (excited) state and E_{ex} is the splitting energy. This is equivalent to applying an external magnetic field to a local spin on a nonmagnetic substrate (blue box represents its energy band). In the case of Kondo screening, whose virtual electron (marked with red balls) tunneling processes are labeled with blue and red arrow connectors for the two spin channels, two spin-split Kondo resonances (marked with a solid green line and a dashed red line) emerge at the Fermi energy. Black arrows correspond to spin directions of energy levels and electrons.

be obtained by lateral tip manipulation, with their mirror axis along one of the crystallographic directions of Pb(111). Because of the moiré pattern, there are two nonequivalent orientations: orientation 1 has Fe[001] direction as the mirror axis direction for the molecule, while orientation 2 does not [Fig. 2(a)].

Spectroscopic measurements on the center of a MnPc molecule reveal a sharp resonance at the Fermi level which is ascribed to a Kondo resonance [13,17]. Figure 2(b) shows typical spectroscopy data of a MnPc molecule with orientation 1. Evidently, the Kondo resonance splits into two peaks, which indicates the molecular spin is magnetically linked to the magnetic substrate. The magnetic origin of the Kondo splitting can be further justified by measuring the spectra of MnPc on the nonmagnetic W(110)-supported Pb islands with the same thickness, where the Kondo resonance does not split any more [18]. We have used two identical Fano resonances with different energy positions [4] to fit the spectroscopic curve of orientation 1 in Fig. 2(b), which yields a Kondo linewidth Γ of 8.0 ± 0.2 meV that corresponds to a Kondo temperature of 92.3 ± 2.3 K and a splitting energy Δ of 16.6 ± 0.2 meV. As the g factor of MnPc on Pb(111) is close to 2 [13], an effective magnetic field of 71.6 ± 0.9 T exerted on the Kondo impurity can be estimated from $\Delta = 2g\mu_B B$, where μ_B is the Bohr magneton. Spectroscopy data of MnPc with orientation 2 show a smaller splitting [as is typically shown in Fig. 2(b)], which can be fitted with a Γ of 9.3 ± 0.3 meV and a Δ of 13.0 ± 0.4 meV [19]. For orientations 1 and 2, statistical measurements over 20 molecules give a Kondo linewidth of 9.0 ± 1.1 meV and 9.8 ± 1.7 meV and a splitting energy of 15.5 ± 2.8 meV and 12.1 ± 2.7 meV, respectively. The different splitting

energy demonstrates that MnPc with orientation 1 has a larger magnetic interaction with the Fe(110) substrate, which is conceivably favored by symmetry match between them.

There are three possible means for realizing such magnetic interactions between the local spin moment and the magnetic substrate, i.e., dipolar interaction, direct exchange interaction, or indirect exchange interaction mediated via conduction electrons in Pb (RKKY interaction). From the amplitudes of Kondo peak splitting and their considerable change with molecular orientations, the magnetic interaction should originate from an exchange field. Furthermore, there is a separation of 3 atomic layers of Pb (8.58 Å) between MnPc and Fe substrate, hindering direct orbital overlap between them. Thus RKKY-type indirect interaction is the most likely mechanism. In this case, an indirect exchange coupling between MnPc and Fe substrate is mediated by the spin-polarized itinerant electrons of the Pb layer in an oscillatory manner with distance (d), which can be described by $J = J_0 \frac{\cos(2k_F d)}{(2k_F d)^D}$, where D is the dimensionality. Because the ratio of the interlayer spacing and the Fermi wavelength of Pb(111) is about 1:4, an antiferromagnetic exchange coupling can be inferred [21]. The RKKY coupling strength here is comparable to direct exchange coupling [7] and is much larger than that between surface-supported magnetic moments which is typically below 1 meV [8,22]. This could be validated from several factors as discussed below. Firstly, in Pb films spin-polarized standing waves form in the surface-normal direction as a result of the spin-dependent confinement and scattering of electrons at the magnetic interface. This enhances the RKKY coupling compared to the conventional case where no electron confinement is present. Secondly, the mediated electrons in Pb are bulk electrons, which provide larger electron density and thus larger coupling strength than that between surface-supported impurity spins where surface state electrons dominate the mediation channel. Thirdly, the dimensionality of RKKY coupling could be close to 1 due to the Fermi surface nesting of Pb(111) [23], diminishing a fast decay of coupling strength with distance.

The physical principle of exchange interaction induced Kondo peak splitting is schematically shown in Fig. 2(c). In a magnetic substrate, the density of states for spin-up and spin-down states are unbalanced (with spin-up states as majority states). A local magnetic impurity would have different interaction strength with the magnetic substrate for different spin channels, which renormalizes the energy position of the unpaired orbital and removes its spin degeneracy [20,24]. Thus the magnetic interaction functions as an effective magnetic field applied to the local spin, similar to an external magnetic field. The ground state of the unpaired spin depends on the sign of exchange interaction: a ferromagnetic interaction promotes the spin-up state as ground state, and an antiferromagnetic interaction generates a spin-down ground state. If the local spin is also screened by the itinerant conduction electrons, two Kondo resonances that are fully spin polarized emerge at $\pm E_{ex}$, i.e., $\pm \frac{\Delta}{2}$, due to the spin and energy conservation of elastic spin-flip scattering [25]. Consequently, both the sign and the strength of the exchange interaction between the local spin and magnetic substrate can directly be extracted from the spin-split Kondo resonances. The spin state of MnPc on Pb cannot be determined from the current study. Assuming $S = 1$ for MnPc according to Ref. [26], the Kondo resonance in this case could possibly originate from an underscreened Kondo channel to a $1/2$ spin. In the presence of RKKY-type exchange coupling to the Fe substrate, the twofold spin degeneracy is removed, which is projected onto the screened Kondo state as a spin-split Kondo resonance.

In order to examine the spin-polarized nature of the split Kondo resonances, we performed spin-polarized STS measurements with a Fe-coated W tip, which readily provides an in-plane spin-sensitive contrast [12,27]. Previous studies have shown that large Fe islands grown on a W(110) substrate have well-defined in-plane domain structures

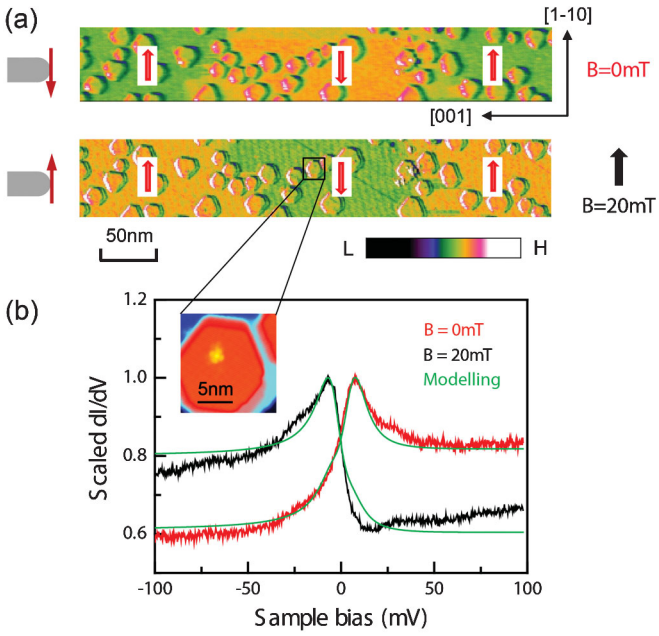

FIG. 3 (color). Spin-polarized STS of MnPc. (a) Spin-polarized STS mapping of a Fe nanostripe decorated with Pb islands showing magnetic contrast at -0.5 V. Magnetization directions of the tip and the domains of the sample are schematically shown. (b) Typical spin-polarized STS spectra of MnPc in orientation 2 [whose image is zoomed from (a) and shown in the inset] measured with a Fe-coated W tip showing spin-resolved split Kondo resonances (tunneling gap: $V = -50$ mV, $I = 0.3$ nA). They have been normalized to unity at the energy position of the Kondo resonances. Green curves are modeled by superposing spin-polarized Kondo resonances and spin-flip spectroscopy.

[28]. Interestingly, we found that Fe stripes capped with a single atomic layer of Pb also exhibit in-plane domains with their magnetization running along the $[1\ -1\ 0]$ direction and the spin contrast can further penetrate through the supported thin Pb islands [Fig. 3(a)]. This provides a reference system for calibrating the magnetization of the tip, which is important for spin-polarized measurements [22]. The microscopic contrast can directly be proven to be spin related with in-field measurements: By applying an in-plane magnetic field of 20 mT along the $[1\ -1\ 0]$ direction, the magnetization of the tip reverses, inducing a contrast reversal of the domain structures [29]; the size of the central domain shrinks, indicating that its magnetization is opposite to the field [Fig. 3(a)].

We zoomed into a Pb island indicated in Fig. 3(a) and performed spectroscopy measurements on supported MnPc molecules before and after the reversal of spin contrast. Typical spectroscopy data of the same MnPc [Fig. 3(b)] shows distinctly different features with the applied field: a prominent Kondo resonance emerges at positive bias of 7.1 mV at 0 mT and shifts to the negative bias side of -6.3 mV at 20 mT, while the spectroscopy data of the Pb substrate does not change significantly. In both cases, only one Kondo resonance can be resolved, which is correlated with the spin contrast mapping of magnetic domains. Thus the two split Kondo resonances are proved to consist of different spin-polarized states. The spin-resolved Kondo resonance of MnPc molecules on Fe stripes with opposite magnetization appears at the opposite side of the Fermi level, which is complementary to the measurement shown in Fig. 3, further supporting the spin-polarized nature of the split Kondo resonance. It is noted that there is some similarity between the shape of the spin-polarized spectrum at 0 T and that of the spin-averaged spectrum of misaligned MnPc on Pb reported in Refs. [26,30]. But they are of very different origin: The former spectrum is dominated by one of the two spin-split Kondo states which depends on its relative alignment with the tip magnetization, while the latter spectrum is essentially a Fano resonance which originates from the interference between the two tunneling channels, i.e., from tip to molecular spin center and to the substrate, and is insensitive to the tip magnetization. We assume the density of states for Fe-coated tips are dominated by majority spin states near the Fermi level based on Ref. [31]. Then the spin character of split Kondo resonances can be determined: the occupied (unoccupied) Kondo resonance is of minority (majority) spin character. This means the RKKY coupling between the MnPc and Fe substrate is antiferromagnetic type, which is consistent with the oscillation phase of RKKY coupling.

We also note that there is an asymmetric background offset in the spectra of Fig. 3(b) for both curves: a step increase in differential conductance occurs on the positive (negative) bias side above the threshold energy of the Kondo resonance at 0 mT (20 mT). The asymmetric background is attributed to spin-polarized spin-flip inelastic tunneling, where tunneling electrons excite the spin state transition of MnPc in the junction by exchanging energy and angular momentum for a sample bias $|V| \geq E_{\mathrm{ex}}/e$. Spin-polarized spin-flip spectroscopy has been demonstrated by Loth *et al.* [32,33] on Mn atoms with a thin insulating CuN film as decoupling layer to prolong the spin lifetime and applied magnetic field of several tesla to lift the spin degeneracy of Mn. In our case, the Mn atom is embedded in a molecular frame, which extends the spin lifetime. Moreover, a large RKKY-type exchange field has removed the spin degeneracy of the local spin states, omitting the application of an external field.

In the presence of a magnetic probe tip, emission and acceptance of tunneling electrons preferentially occur for one spin channel. This will enhance or suppress the inelastic spin-flip electron tunneling through MnPc, depending on the spin orientation of tunneling electrons [33]. We take the spin-up state being the ground state of MnPc spin, for example. When the tip magnetization is spin-down, it can provide the required electrons for effectively promoting spin-flip excitations of the local spin. However, when electrons tunnel from sample to tip, spin-flip scattering can generate a tunneling current with spin-up polarization by selectively passing spin-up electrons and flipping spin-down electrons, which is incompatible with the tip magnetization. As a result, the differential conductance of MnPc exhibits an asymmetric step at $+E_{\mathrm{ex}}/e$ with higher intensity on the positive bias side [Fig. 3(b), red curve]. Similarly, a tip with spin-up magnetization cannot provide but can accept the tunneling electrons with the desired spin orientation, which induces an asymmetric step at $-E_{\mathrm{ex}}/e$ with higher intensity on the negative bias side [Fig. 3(b), black curve] [18]. The inelastic spin-flip spectroscopy functions thereby as a spin filter for generating spin-polarized tunneling electrons. A modeling [18] based on the superposition of spin-polarized Kondo resonance and spin-flip inelastic tunneling spectroscopy (with $\Delta = 9.5$ meV, $\Gamma = 8$ meV, Fano factor $q = -10$) could reasonably reproduce the shape of the spin-resolved differential conductance spectra [Fig. 3(b), green curve] [34]. From the modeling, the tip spin polarization is estimated to be ~ 0.6, which is consistent with the high spin polarization of Fe tips at the Fermi energy (up to ~ 0.7 as calculated in Ref. [31]).

In summary, we have devised a Kondo system which is exchange coupled to a magnetic substrate through RKKY interaction. Given the oscillatory nature of RKKY interaction, our method provides a more general platform for tailoring the exchange coupling through precise film thickness control [35], which is compatible with current nanotechnology. The current system of a local spin exchange coupled to a magnetic substrate can extract spin-polarized tunneling electrons not only from elastic tunneling through

the spin-split Kondo resonances at $\pm E_{ex}$, but also from inelastic spin-flip tunneling at a wide energy range ($|E| \geq E_{ex}$). The nanometer scale spin polarizer does not need the presence of an external magnetic field and can be controlled by changing the magnetization of the magnetic substrate.

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