



## Exchange Interaction between Single Magnetic Adatoms

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(Received 27 October 2006; published 29 January 2007)

The magnetic coupling between single Co atoms adsorbed on a copper surface is determined by probing the Kondo resonance using low-temperature scanning tunneling spectroscopy. The Kondo resonance, which is due to magnetic correlation effects between the spin of a magnetic adatom and the conduction electrons of the substrate, is modified in a characteristic way by the coupling of the neighboring adatom spins. Increasing the interatomic distance of a Cobalt dimer from 2.56 to 8.1 Å we follow the oscillatory transition from ferromagnetic to antiferromagnetic coupling. Adding a third atom to the antiferromagnetically coupled dimer results in the formation of a collective correlated state.

DOI: [10.1103/PhysRevLett.98.056601](https://doi.org/10.1103/PhysRevLett.98.056601)

PACS numbers: 72.15.Qm, 68.37.Ef, 72.10.Fk, 75.20.Hr

The magnetic properties of nanostructures play a pivotal role in the design of miniaturized spin-based devices. One of the key parameters is the magnetic interaction between the constituent atoms of a nanostructure. This interaction can be due to direct or indirect coupling as well as mediated via a supporting substrate or host. Depending on the strength and sign of the exchange interaction, the nanostructure can be driven into ferromagnetic or antiferromagnetic behavior, a correlated state or complex spin structures [1]. However, up to now it was impossible to measure experimentally the magnetic interaction between individual atoms. Only recently spin-flip experiments by Hirjibehedin and co-workers [2] have enabled a direct probing of the magnetic interaction in linear manganese chains decoupled from the substrate by a spacer layer. In the present Letter we exploit the Kondo effect as a local probe to determine the exchange interaction between individual cobalt adatoms on a metallic substrate as a function of their distance. This approach was originally proposed by Chen *et al.* [3]. Their experiment, however, did not allow for an assessment of the exchange coupling, because for the studied nearest neighbor dimers on Au(111) only the disappearance of the Kondo resonance was observed.

The Kondo effect originates from the screening of the spin of a magnetic impurity by the surrounding conduction band electrons [4] and is characterized by a strong peak in the impurity's density of states near the Fermi level. This many body resonance has been observed for single magnetic adatoms [5–7], in artificial nanostructures such as quantum corrals [8], and for molecules [9,10]. In scanning tunneling spectroscopy (STS) spectra, it shows up as a feature which can be described by a Fano line shape [11–13]. From a fit, the peak width  $\Gamma$  is obtained which is the characteristic energy scale—the Kondo temperature  $T_K$ —of the impurity system. For the Kondo scenario of a single

magnetic impurity on a nonmagnetic metal surface a quantitative description has been proposed [14].

As a second impurity is brought into proximity, magnetic interactions between the impurities become important and may modify the Kondo resonance considerably. These magnetic interactions can be of different origin: magnetic dipolar coupling, direct exchange between the impurities due to an overlap of the impurity  $d$  orbitals, or finally the Ruderman-Kittel-Kasuya-Yosida (RKKY) interaction. The latter is an indirect spin-spin interaction mediated by the conduction electrons of the host. Here, we demonstrate that it is possible to determine the magnetic interaction between single magnetic atoms adsorbed on a noble metal surface by measuring the modified Kondo spectrum. The results are compared to theoretical predictions of the magnetic interactions between single atoms [15]. The evolution of the Kondo line shape obtained by STS upon varying the interatomic distance between Co adatoms in dimer and trimer configurations on a Cu(100) single crystal surface is compared to many body theory, which allows us to determine the magnetic coupling as function of the interatomic spacing. Since manipulation of atoms on (100) metal surfaces is difficult due to a high energy barrier between neighboring sites, dimers with well-defined interatomic distance have been fabricated with an alternative approach. First, cobalt carbonyl complexes are formed [10], in which the CO ligands inhibit nucleation and island formation and facilitate the growth of one-dimensional structures. Once these structures are grown, the CO ligands can be removed by tip-induced dissociation of the molecules leaving behind on the surface only the cobalt atoms. The panels in Fig. 1(a) show different cobalt dimer configurations prepared as described above with interatomic distances between the neighboring cobalt atoms ranging from 2.56 to 8.1 Å together with the

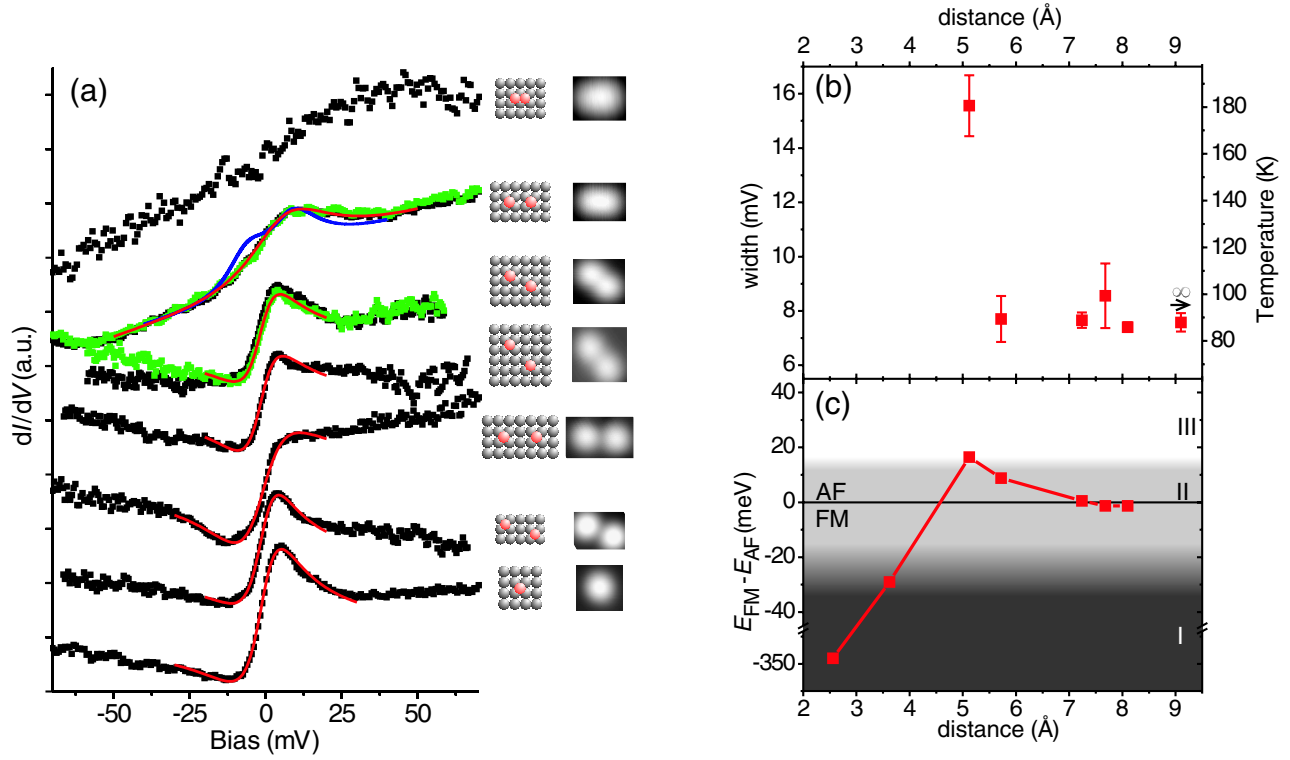


FIG. 1 (color online). Kondo resonance of cobalt dimers on Cu(100) measured by STS at 6 K. As a consistency check, spectra taken on both ends of the dimers are shown (green and black dots) to be equivalent. (a) Model, topography, and spectra for (from top to bottom) a compact dimer (2.56 Å), a dimer at 5.12, at 5.72, at 7.24, at 7.68, at 8.10 Å, and for a single adatom at infinite distance ( $> 20$  Å) are depicted. The spectra are shown together with fits of a Fano function (red solid line), for the dimer at 5.12 Å also a simulated curve according to Eq. (1) with  $J = 15$  meV and  $\Gamma = 1.2T_K^0$  is plotted (blue solid line). For the dimer at 5.12 Å, a linear background had to be taken into account to obtain a reasonable fit for a Fano function (spectra shifted vertically for clarity). (b) The width of the resonance as a function of distance, and (c) KKR calculations for the exchange interaction between cobalt adatoms on Cu(100) [15]. The three distinct regimes discussed in the text are shaded in different grays.

corresponding STS spectra. For the compact dimer the interaction between the spins is much stronger than the coupling to the substrate and the Kondo effect (at 6 K) is suppressed. For the next-nearest neighbor distance, however, a resonance is found at the Fermi energy. The resonance is considerably broader than that of a single cobalt adatom. By fitting the STS signal with a single Fano line shape, we extract that the energy width of the feature would correspond to a Kondo temperature  $T_K = 181 \pm 13$  K. For distances of 5.72 and 7.24 Å, the Kondo resonance has already recovered almost the same width and line shape as that of a single cobalt adatom. For even larger distances, the same width as on an adatom is restored. The widths of the resonances are tabulated in Table I and summarized in Fig. 1(b).

Our data can be theoretically interpreted as a realization of a two-impurity Kondo problem [16]. Depending on the relative strength of the exchange interaction compared to the single-impurity Kondo temperature  $T_K^0$ , the dimers enter different regimes. For a strong ferromagnetic exchange interaction  $|J| \gg T_K^0$  [marked as regime I in Fig. 1(c)] a correlated state with a new Kondo temperature

$T_K^{\text{dimer}} \approx (T_K^0)^2/|J|$  will occur [16]. This new Kondo scale is much lower than the temperature of the experiment and can therefore not be detected in our measurements. For intermediate exchange interaction  $J$  [regime II in Fig. 1(c)], the single-impurity Kondo resonance is recovered. Finally, for a sufficiently strong antiferromagnetic exchange interaction  $J > J^* \sim 2T_K^0$  [marked as regime III in Fig. 1(c)] between neighboring magnetic atoms, the Kondo resonance is split and a singlet state is formed between the impurities [17]. This singlet state is characterized in the impurity density of states by peaks located at energies  $\pm J/2$  [18–20]. The splitting of the Kondo resonance for strong antiferromagnetic coupling has been observed previously in quantum dots coupled either by a direct tunnel junction [21] or by an indirect RKKY interaction mediated via another large quantum dot [22]. For adatoms on a substrate, we can show using a slave boson mean field theory approach as in Ref. [19] that this splitting generates the following density of states:

$$\rho(\varepsilon) \propto a_1 f\left(\frac{\varepsilon + J/2}{\Gamma}, q\right) + a_2 f\left(\frac{\varepsilon - J/2}{\Gamma}, q\right), \quad (1)$$

TABLE I. Width, position  $\varepsilon_K$ , and line shape parameter  $q$  of a single Fano resonance fit to the feature of Cobalt adatoms, dimers, and trimers on Cu(100) measured by STS at 6 K. For dimers and trimers, the interatomic distances  $d$  and for the trimer the data for both features at the Fermi energy are given (monomer value taken from Ref. [7]). The errors given are the standard deviation of averages over measurements taken on different adatoms pairs and with different tips.

|         | $d$ (Å) | Width (meV)      | $\varepsilon_K$ (meV) | $q$              |
|---------|---------|------------------|-----------------------|------------------|
| Monomer | -       | $7.58 \pm 0.34$  | $-1.3 \pm 0.4$        | $1.13 \pm 0.06$  |
| Dimer   | 2.56    | -                | -                     | -                |
| Dimer   | 5.12    | $15.6 \pm 1.1$   | $5.3 \pm 1.6$         | $3.2 \pm 1.1$    |
| Dimer   | 5.72    | $7.71 \pm 0.85$  | $-0.95 \pm 0.73$      | $1.56 \pm 1.04$  |
| Dimer   | 7.24    | $7.66 \pm 0.28$  | $-0.93 \pm 0.70$      | $1.17 \pm 0.14$  |
| Dimer   | 7.68    | $8.89 \pm 1.57$  | $-0.94 \pm 1.20$      | $1.10 \pm 0.48$  |
| Dimer   | 8.1     | $7.40 \pm 0.18$  | $-0.72 \pm 0.14$      | $1.44 \pm 0.04$  |
| Trimer  | 5.12    | $13.23 \pm 0.91$ | $-1.43 \pm 0.76$      | $27.2 \pm 0.3$   |
|         |         | $11.93 \pm 1.15$ | $-0.69 \pm 0.72$      | $-0.03 \pm 0.01$ |

where  $f(x, q) = \frac{(x+q)^2}{x^2+1}$  and  $a_1 \sim a_2$ . This equation describes two Fano resonances at  $\pm J/2$  with a width  $\Gamma$  which is of the same order as the single-impurity one. The resonances are resolved in the tunneling spectrum as only one broadened feature as observed in the experiment due to the width of the resonances, which is of the same order as the splitting. Thus the width of the resonance in this case provides a measure for the magnetic interaction between the adatoms.

In Table I, the experimental results for the atomic arrangements which have been investigated are summarized. For the compact dimer (2.56 Å), we find that the Kondo resonance disappears. This is consistent both with previous experiments on Co dimers on Au(111) by Chen *et al.* [3], and the strong ferromagnetic coupling predicted by *ab initio* calculations [15], which introduces a Kondo scale  $T_K^{\text{dimer}} \sim 2$  K for the nearest neighbor dimer, which is smaller than the temperature of the experiment. The spectrum on the next-nearest neighbor dimer (5.12 Å) shows a distinct Kondo resonance at the Fermi level, which is broadened compared to the spectrum of the isolated Co adatom. By using Eq. (1) to fit the experimental data, we extract an antiferromagnetic coupling  $J$  of about 16 meV. The broadened spectrum can be rationalized by an antiferromagnetic coupling between the two Co adatoms. The relevant Kondo energy scale is  $k_B T_K = 7.58$  meV for a Co atom on Cu(100) [15]. The magnetic interactions are thus large enough to induce a splitting of the Kondo effect but sufficiently small to prevent complete quenching as observed for the compact dimer. At larger interatomic distances the spectrum and  $T_K$  transforms back to the single adatom value, with the exception of an interatomic distance of 7.68 Å, where the resonance width has a local maximum as a function of distance. According to *ab initio* calculations [15], the interaction between two cobalt ad-

toms on Cu(100) is mainly due to RKKY interactions. When the adatoms are on next-nearest neighbor sites, Stepanuyk *et al.* predict an antiferromagnetic interaction of about 17 meV. This is in excellent agreement with the estimation we obtain assuming a split Kondo resonance. When the adatoms are further apart (5.72 Å), the calculations predict that the RKKY interaction is reduced to 8 meV, which is not large enough to split the Kondo resonance and therefore explains why the usual single-impurity Kondo resonance is almost recovered.

Besides cobalt dimers, we studied a linear trimer. Trimers of magnetic adatoms have been studied previously by Jamneala *et al.* [23]. Their study focused on compact Cr trimers, no statement was made on the low energy excitations of a linear trimer. Our trimer has the adatoms on next-nearest neighbor sites as shown in Figs. 2(a) and 2(b). The trimer has been prepared in a similar way as the dimers. The tunneling spectra change qualitatively on the trimer. As can be seen from Fig. 2(c), the spectra show a superposition of features—resulting in two maxima and a dip in between them.

In order to understand the STS spectra for the linear trimer, we study theoretically within a slave boson mean field theory (SBMFT) [1] and perturbative renormalization group (PRG) theory [24] a cluster of three inline magnetic impurities coupled to a conduction band. As for the dimer, two scenarios are possible: Either the RKKY interaction is not strong enough to split the Kondo resonances ( $J \sim 2T_K^0$ ) and the middle impurity and side impurities have their own Kondo resonances of different widths or the RKKY interaction is sufficiently strong to induce a collective magnetic behavior ( $J \gtrsim 2T_K^0$ ). In the latter case, the SBMFT predicts three Fano features centered at  $eV = 0, \pm J/2$ . Additionally, for strong antiferromagnetic interaction the ground state has a net spin which is screened at low temperatures giving therefore rise to an extra Kondo resonance around zero bias. This extra Kondo resonance is not captured by

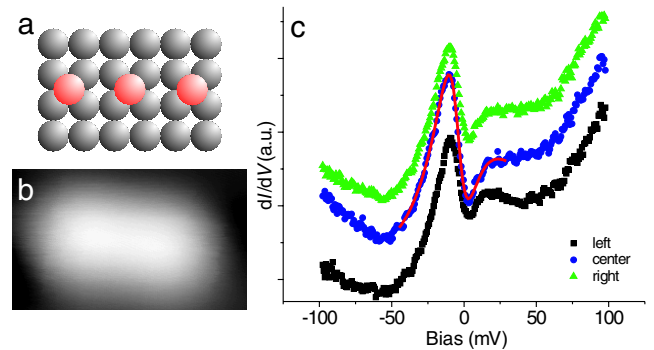


FIG. 2 (color online). Kondo resonance of the Cobalt trimer on Cu(100) measured by STS at 6 K. (a) Model of the trimer investigated. (b) STM topography (same scale as model). (c) Spectra taken on the left, right, and center atom, the spectra are shifted vertically. The solid line is a fit to a double Fano resonance.

SBMFT. An analysis similar to the one developed by Lazarovits *et al.* [24] based on PRG indicates that the width of this resonance can be of order of  $T_K^0$  or even larger.

In the first case, the STS signal is a sum of two single-impurity Fano resonances whose amplitudes depend on the position of the STM tip along the cluster. In the second case, the STS signal can be understood as the sum of two Fano resonances centered around zero bias plus a dimer (split) Fano resonance at  $eV = \pm J/2$ . Since in both cases at least two zero-bias features are predicted, we fit our data with two Fano resonances. The values we obtain are also given in Table I. In order to discriminate between both scenarios, we have analyzed the spatial dependence of the relative amplitude of both zero-bias features. We find a negligible dependence of the line shape on the tip position especially when moving the tip away from the chain. This clearly favors the second scenario where both zero-biased resonances are collective features. This conclusion is consistent with the calculated strength of the magnetic interaction in the trimer. We have performed calculations employing the Korringa-Kohn-Rostoker Green's-function method (KKR) (as described in [25]) which reveal an energy difference between the ferromagnetic and the anti-ferromagnetic configuration of the trimer of 35 meV [25]. This yields a nearest-neighbor (NN) spin interaction in the trimer of  $J_{NN} \sim 17$  meV (comparable to the dimer value), which is larger than  $T_K^0$  and puts the trimer in the correlated regime. While for chains consisting of Mn atoms decoupled from the metallic substrate as studied by Hirjibehedin *et al.* [2] collective magnetic excitations have been observed, the correlated electronic state found here is induced by the coupling of the magnetic atoms via the substrate.

The situation in the Co chain also differs from the compact Cr trimer studied by Jamneala *et al.* [23] where the magnetic exchange interactions between the adatoms have been shown to be several orders of magnitude larger than the Kondo temperature of a single Chromium adatom leading to different behaviours depending very strongly on the shape of the trimer [24].

In conclusion, we have shown how the magnetic interaction between single magnetic atoms coupled to a substrate can be determined via the Kondo effect. Understanding and being able to measure the magnetic coupling on the single atom level is expected to play a key role in the design of magnetoelectronic devices. Magnetic nanostructures with specific properties can be tailored by controlling and manipulating the exchange interaction. Furthermore, the transition from a single-impurity Kondo effect to a collective state of a small chain or cluster offers a unique opportunity to compare theories for the 1D Kondo chain to experimental model systems.

P.S. has been partially supported by the contract PNANO "QuSpins" of the french ANR.

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