

Disappearance of the Kondo resonance for atomically fabricated cobalt dimers

W. Chen,* T. Jamneala,† V. Madhavan, and M. F. Crommie†

Department of Physics, Boston University, 590 Commonwealth Avenue, Boston, Massachusetts 02215

(Received 8 June 1999)

We have used scanning tunneling spectroscopy and atomic manipulation to study the interaction between a single pair of magnetic atoms at the surface of a nonmagnetic metal. The local electronic structure of cobalt adatoms on Au(111) was measured for different cobalt-cobalt interatomic spacings at $T=6$ K. Artificially fabricated cobalt dimers are found to show an abrupt disappearance of the Kondo resonance for cobalt-cobalt separations less than 6 Å. This behavior is explained as the result of reduced exchange coupling between gold conduction electrons and ferromagnetic cobalt dimers. [S0163-1829(99)50436-0]

The magnetic properties of microscopic structures are largely determined by interatomic interactions.^{1,2} These interactions include short-range bonding and exchange mechanisms,³ as well as longer-range indirect coupling.⁴ Effects of such interactions have been seen in ensembles of magnetic atoms^{5,6} and molecules,⁷ and isolated mesoscopic clusters,^{8,9} but little has been done to directly probe interactions in magnetic structures at the atomic scale. One way of obtaining this kind of information is through the Kondo effect.¹⁰ The Kondo effect occurs when a magnetic impurity in a metal couples to surrounding conduction electrons. At temperatures below a characteristic Kondo temperature (T_K), this coupling causes conduction electrons to form a highly correlated ground state that screens the magnetic moment of the impurity and leads to a narrow Kondo resonance at the Fermi energy (E_F).¹⁰ Interactions between magnetic atoms are expected to change the behavior of a Kondo system. Indirect exchange coupling between a single pair of Kondo impurities has been predicted to modulate the Kondo effect and even lead to novel non-Fermi liquid behavior.^{11,12} Direct coupling between magnetic impurities is predicted to result in a variety of magnetic ground states that should strongly affect Kondo behavior for small clusters.^{1,13-15} Recent scanning tunneling microscope (STM) observations of the Kondo effect for single magnetic atoms^{16,17} raise the possibility of directly studying such interaction effects at the atomic lengthscale.

Here we report an experimental study of the interaction between two individual magnetic atoms at the (111) face of a clean gold crystal. A cryogenic STM was used to perform local spectroscopic measurements on two cobalt atoms held at different interatomic separation distances. The distance between the two atoms was varied by moving the atoms directly with the tip of the STM. We find that the spectrum of low-energy magnetic excitations observed for an isolated cobalt atom (the Kondo resonance¹⁰) disappears when two cobalt atoms are brought together into a dimer configuration. This behavior is best explained as the result of reduced coupling between the magnetic moment of a ferromagnetic cobalt dimer and surrounding conduction electrons.

Our measurements were performed using a homebuilt STM contained in ultra-high-vacuum (UHV) and cooled to 6 K. The single-crystal Au(111) substrate was cleaned in UHV by repeated cycles of Ar-ion sputtering and annealing. The

Au(111) surface was then cooled to 6 K and dosed in UHV with a calibrated cobalt evaporator (typical coverages were 0.003 monolayer). dI/dV spectra were measured through lockin detection of the ac tunnel current driven by a 450 Hz, 1 mV (rms) signal added to the junction bias.

The interaction between a single pair of cobalt atoms was studied by first performing local spectroscopic measurements on two well-separated cobalt atoms. The atoms were then moved closer together in increments, with both atoms undergoing spectroscopic survey at each separation. The central experimental result of this paper is that the Kondo resonance for cobalt surface impurities does not depend on the distance between cobalt atoms *until* the atoms are brought together to an interatomic distance less than 6 Å. Once two cobalt atoms are in this “dimer” configuration, the Kondo resonance abruptly disappears for both atoms.

Figure 1 shows an STM image of the process of positioning two cobalt atoms at varying interatomic distances of 15, 9, and approximately 4 Å. The cobalt atoms were slid along the Au(111) surface using the tip of an STM as described in Ref. 18. The current/voltage parameters used for sliding cobalt atoms on Au(111) were typically 50 nA/10 mV. The smallest interatomic separation at which individual atoms could be resolved was 6 Å. At closer separations the cobalt-cobalt interatomic distance is difficult to determine, since the STM topograph shows only a single, merged dimer. Figure 2 shows a topographic image of a cobalt dimer with a cobalt monomer in close proximity. A rough estimate of the separation between the atoms in the dimer can be made by fitting a Gaussian curve to the monomer profile and then fitting a sum of two such curves to the dimer profile. The distance between Gaussians which yields the best fit is then taken as the interatomic spacing. Using this criterion, we estimate that the distance between atoms in the dimer shown in Fig. 2 is $4.3 \text{ Å} \pm 0.5 \text{ Å}$.

Local spectroscopic measurements were performed by holding the tip of the STM stationary over different sites on the surface and measuring the bias dependence of the tunnel junction differential conductivity (dI/dV). This quantity yields a measure of the energy dependence of the electronic local density of states at the spot just beneath the STM tip.^{16,17} The top curve in Fig. 3 shows the dI/dV spectrum measured while holding the tip stationary over a bare patch of the Au(111) surface. This spectrum is relatively feature-

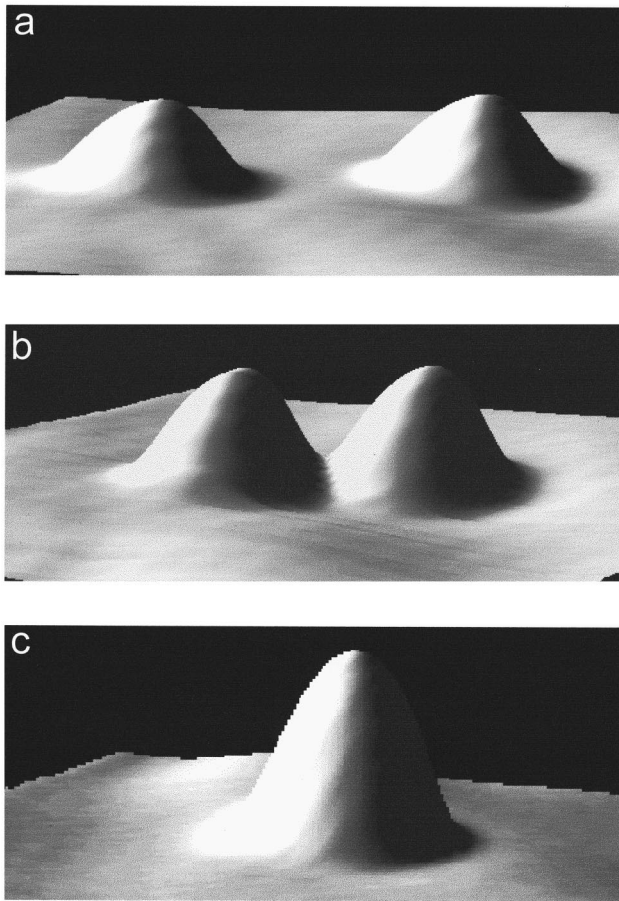


FIG. 1. Process of building a cobalt dimer from two individual cobalt atoms on the surface of Au(111) (constant current STM imaging parameters: $I=5 \times 10^{-9}$ A, $V=0.1$ V). (a) The atoms initially are 15 Å apart (center-to-center). (b) The atoms after being repositioned with the STM tip to a separation of only 9 Å. (c) The atoms after being positioned into the final dimer configuration (approximate separation is 4 Å).

less as the energy is swept through E_F ($V=0$). The second curve in Fig. 3 shows the dI/dV spectrum measured while holding the STM tip stationary over the center of an isolated cobalt atom on the gold surface. Here a narrow, asymmetric resonance can be seen near E_F . This is the Kondo resonance for a single cobalt atom.¹⁶ (This feature has also been interpreted as a ‘bare’ d resonance,¹⁹ but we believe the width is too narrow for this to be the case.¹⁶) The width of the resonance yields $T_K=70$ K, and the energy asymmetry is explained by the fact that the Kondo resonance is expressed via a Fano line shape.^{16,17} Spectra measured on different cobalt atoms did not deviate significantly from this curve for inter-cobalt separations ranging from hundreds of Å down to 6 Å. At separations less than 6 Å, however, cobalt atoms merge into a dimer and their electronic properties change dramatically. The third curve in Fig. 3 shows the dI/dV spectrum measured with the STM tip held stationary over an atomically fabricated cobalt dimer. The Kondo resonance has disappeared. This abrupt disappearance of the Kondo resonance was seen consistently in spectra obtained from cobalt dimers using different STM tips (different tips were obtained through field emission and controlled collision with the surface).

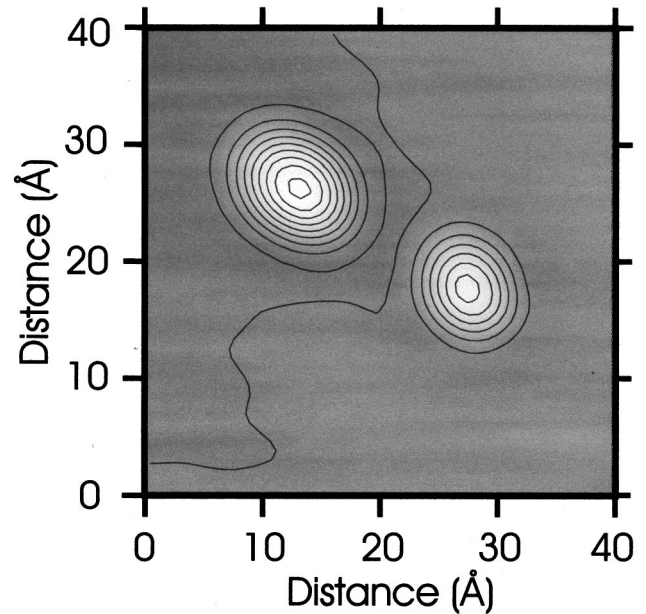


FIG. 2. Constant current STM topograph of a fabricated cobalt dimer (upper left) positioned near a single cobalt atom. Height gradient is 0.1 Å per contour. Imaging parameters: $I=5 \times 10^{-9}$ A, $V=0.1$ V.

The disappearance of the Kondo resonance is a signature of the interaction between two cobalt atoms at the gold surface. In order to understand this interaction, we must address the different possible interaction mechanisms. The three most likely mechanisms are as follows: (1) quenching of the dimer magnetic moment, (2) antiferromagnetic coupling between the cobalt atoms, (3) reduction of the exchange coupling between the dimer magnetic moment and surrounding conduction electrons. Here we discuss these mechanisms and argue why we believe that the third mechanism is the one that accurately describes the behavior of a cobalt dimer on Au(111).

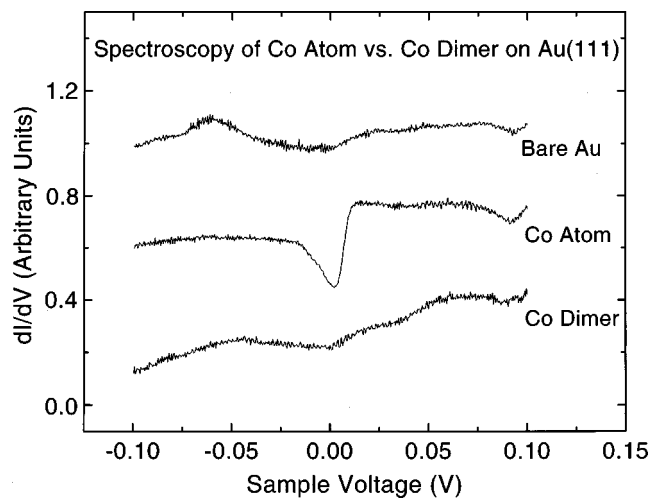


FIG. 3. dI/dV spectra obtained with the STM tip held over a single cobalt atom, an atomically fabricated cobalt dimer, and the clean gold surface (curves have been shifted vertically). The Kondo resonance can be seen for the individual cobalt atom, but is no longer present for the cobalt dimer. $dI/dV=5 \times 10^{-8} \Omega^{-1}$ for all three spectra at $V=0.100$ V (the amplitude of the Kondo resonance reflects a 26% change in dI/dV for the single-atom spectrum).

Magnetic moments tend to form only when the electronic structure of an object satisfies the Stoner criterion, $\rho(E_F)U > 1$ [where $\rho(E_F)$ is the density of states at E_F and U is the electronic correlation energy].²⁰ It is conceivable that a single impurity atom might satisfy the Stoner criterion while a dimer does not,²¹ thereby resulting in a quenched magnetic moment/atom for a dimer and no dimer Kondo effect. Weak localization measurements, however, imply that neighboring cobalt atoms at the surface of gold are magnetic. This is supported by local-spin-density (LSD) functional calculations for cobalt dimers at the surfaces of Cu(100),¹⁵ Ag(100),¹⁴ and Au(100),²² all of which predict a robust cobalt moment of almost $2\mu_B$ /atom. Quenching of the magnetic moment is therefore not a likely cause for the disappearance of the Kondo resonance in cobalt dimers.

The next possibility is antiferromagnetic (AF) coupling. Strong AF coupling between the cobalt atoms of a dimer should yield a net singlet ground state (the total dimer spin then being equal to 0), thus “turning off” the Kondo effect and removing the Kondo resonance.²³ AF coupling can arise from either direct or indirect coupling mechanisms. We first consider the possibility of indirect AF coupling. The Kondo effect is predicted to quench when indirect coupling [also known as Rudman-Kittel (-Kasuya)-Yoshida (RKKY) coupling⁴] is much stronger than the Kondo binding energy, kT_K .¹¹ These energies can be estimated. The RKKY coupling energy between two magnetic impurities separated by a distance r in the bulk of a metal can be written as⁴

$$U_{\text{RKKY}}(r) = \frac{3}{8\pi} \frac{(J\nu)^2}{E_F} n k_F^3 \frac{[\sin(2k_F r) - 2k_F r \cos(2k_F r)]}{(2k_F r)^4}. \quad (1)$$

Here n is electron density, k_F is the Fermi wave vector, ν is the volume of a unit cell, and J is the “ s - d ” exchange constant which represents the coupling strength between conduction electrons and the magnetic moment of a cobalt atom. Assuming cobalt atoms to have a net spin ≈ 1 ,^{13,19} the Kondo binding energy can be written as

$$kT_K \approx D |3\rho_0 J \nu|^{1/3} \exp\left(\frac{1}{3\rho_0 J \nu}\right) \quad (2)$$

within the Coqblin-Schrieffer model¹⁰ (here D is the bandwidth of gold and ρ_0 is the local density of states at E_F). Using $T_K = 70$ K, Eq. (2) yields a value of $J = -0.1$ eV. This can then be used in Eq. (1) to obtain an antiferromagnetic maximum of $|U_{\text{RKKY}}| = 0.2$ mV for a separation of π/k_F between cobalt atoms. We are thus in the limit $|U_{\text{RKKY}}| \ll kT_K$, making RKKY coupling an unlikely cause for the disappearance of the Kondo resonance in cobalt dimers. This three-dimensional calculation is not strictly valid for cobalt atoms at a surface, but we take it as a rough bound on the magnitude of U_{RKKY} (surface-state contributions lead to an incorrect AF coupling distance, and so are not considered).

Direct AF interaction between impurities must be considered as a possibility when the impurities are in close proximity (i.e., close to nearest-neighbor spacing). The Alexander-Anderson (AA) model addresses this regime by treating a pair of magnetic atoms as idealized Anderson im-

purities with an added interatomic electronic hopping term.²⁴ The AA model implies that if E_F lies midway between the spin-split d resonances of a single impurity, then AF coupling is favored for a pair of atoms. If E_F lies close to the minority d resonance, on the other hand, the tendency is toward ferromagnetic (FM) coupling. Since cobalt adatoms are expected to have a d -level filling on the order of 8 electrons,^{13,19} E_F must intersect the minority spin manifold. FM coupling is thus the most likely ground state for a cobalt dimer. This conclusion is supported by the fact that LSD calculations for free cobalt dimers,³ cobalt dimers in the bulk of Ag,²⁵ and cobalt dimers at the surfaces of Ag(100) (Ref. 14) and Au(100) (Ref. 22) all yield a FM dimer ground state. Weak localization measurements, as well, imply that neighboring cobalt atoms on gold couple ferromagnetically.⁶ Direct AF coupling is thus an unlikely explanation for the disappearance of the Kondo resonance in cobalt dimers.

The most likely reason for the Kondo resonance disappearance is a reduction in the exchange coupling between gold conduction electrons and cobalt impurities in the dimer configuration. As seen in Eq. (2), the Kondo temperature of a magnetic scatterer depends exponentially on the coupling, J . This makes it possible for only a small reduction in J to drop T_K below the experimental temperature of 6 K, thus causing the Kondo resonance to disappear for a dimer. To see that this is a plausible scenario, one can consider the Schrieffer-Wolff expression for J :¹⁰

$$J \approx \frac{2V^2 U}{(\varepsilon_d - E_F)(\varepsilon_d + U - E_F)}. \quad (3)$$

Here ε_d is the bare d -orbital energy and V is the hybridization matrix element coupling conduction electrons to the impurity d orbital. This perturbational expression is derived only for a spin- $\frac{1}{2}$ impurity, but we expect the physical trends to be true under more general circumstances.²⁶ J is seen to decrease when either V or U is reduced, and also when the spin-split d resonances shift away from the Fermi energy. V and U are not expected to change strongly upon dimer formation, but the AA model implies that the minority d resonance splits away from E_F for a FM dimer.^{24,25} Such a shift of d orbital states away from E_F should lead to a reduction in J and, hence, a reduction of T_K for cobalt dimers (thus driving down the dimer Kondo resonance). This interpretation is also consistent with magnetic susceptibility results for Au-Co alloys that suggest a large reduction in T_K for cobalt dimers versus cobalt monomers in the bulk of gold.⁵

The interaction between cobalt atoms is thus seen to be driven by the direct overlap of $3d$ orbitals between adjacent atoms (such behavior is expected to be reduced in rare-earth impurities since $4f$ orbitals are more tightly bound). Our analysis has relied on simple, intuitive ideas based on spin- $\frac{1}{2}$ behavior to understand the disappearance of the Kondo resonance for dimers. For a more accurate description of interacting cobalt impurities, one should take into account the multi-channel nature of this Kondo system²⁶ (due to the fact that each cobalt atom has more than one electron in the d orbital). The ideas presented here may be further tested by

performing experiments at lower temperature to observe the Kondo peak that is expected to exist for cobalt dimers at reduced temperature.

We gratefully acknowledge V. S. Stepanyuk, P. H. Deder-

ichs, P. Mavropoulos, and B. A. Jones for extremely useful discussions. This work was supported by NSF Grants Nos. DMR-9457955 and DMR-9503837, and by the W. M. Keck Foundation.

*Present address: Condensed Matter Physics, Caltech 114-36, Pasadena, CA 91125.

†Present address: Dept. of Physics, University of California at Berkeley, Berkeley, CA 94720.

¹K. Wildberger, V. S. Stepanyuk, P. Lang, R. Zeller, and P. H. Dederichs, Phys. Rev. Lett. **75**, 509 (1995).

²B. V. Reddy and S. N. Khanna, Phys. Rev. B **45**, 10 103 (1992).

³I. Shim and K. A. Gingerich, J. Chem. Phys. **78**, 5693 (1983).

⁴K. Yoshida, *Theory of Magnetism* (Springer, New York, 1996).

⁵E. Boucai, B. Lecoanet, J. Pilon, J. L. Tholence, and R. Tournier, Phys. Rev. B **3**, 3834 (1971).

⁶H. Beckmann and G. Bergmann, Phys. Rev. B **54**, 368 (1996).

⁷J. R. Friedman, M. P. Sarachik, J. Tehada, and R. Ziolo, Phys. Rev. Lett. **76**, 3830 (1996).

⁸J. Shi, S. Gider, K. Babcock, and D. D. Awschalom, Science **271**, 937 (1996).

⁹W. Wernsdorfer, E. Bonet Orozco, K. Hasselbach, A. Benoit, D. Mailly, O. Kubo, H. Nakano, and B. Barbara, Phys. Rev. Lett. **79**, 4014 (1997).

¹⁰A. C. Hewson, *The Kondo Problem to Heavy Fermions* (Cambridge University Press, Cambridge, 1993).

¹¹C. Jayaprakash, H. R. Krishna-Murthy, and J. W. Wilkins, Phys. Rev. Lett. **47**, 737 (1981).

¹²K. Ingersent, B. A. Jones, and J. W. Wilkins, Phys. Rev. Lett. **69**, 2594 (1992).

¹³P. Lang, V. S. Stepanyuk, K. Wildberger, R. Zeller, and P. H. Dederichs, Solid State Commun. **92**, 755 (1994).

¹⁴V. S. Stepanyuk, W. Hergert, P. Rennert, K. Wildberger, R. Zeller, and P. H. Dederichs, Phys. Rev. B **54**, 14 121 (1996).

¹⁵V. S. Stepanyuk, W. Hergert, P. Rennert, K. Wildberger, R. Zeller, and P. H. Dederichs, J. Magn. Magn. Mater. **165**, 272 (1997).

¹⁶V. Madhavan, W. Chen, T. Jamneala, M. F. Crommie, and N. S. Wingreen, Science **280**, 567 (1998).

¹⁷J. Li, W.-D. Schneider, R. Berndt, and B. Delley, Phys. Rev. Lett. **80**, 2893 (1998).

¹⁸D. M. Eigler and E. K. Schweizer, Nature (London) **344**, 524 (1990).

¹⁹M. Weissmann, A. Saul, A. M. Llois, and J. Guevara, Phys. Rev. B **59**, 8405 (1999).

²⁰P. W. Anderson, Phys. Rev. **124**, 41 (1961).

²¹B. V. Reddy, M. R. Pederson, and S. N. Khanna, Phys. Rev. B **55**, R7414 (1997).

²²V. S. Stepanyuk *et al.* (unpublished).

²³M. T. Beal-Monod, Phys. Rev. **178**, 878 (1969).

²⁴S. Alexander and P. W. Anderson, Phys. Rev. **133**, A1594 (1964).

²⁵A. Oswald, R. Zeller, P. J. Braspenning, and P. H. Dederichs, J. Phys. F **15**, 193 (1985).

²⁶Ph. Nozières and A. Blandin, J. Phys. (Paris) **41**, 193 (1980).