man & Allanheld, Totowa, NJ, 1984).
11. E. S. Morgan, *American Slavery, American Freedom, the Ordeal of Colonial Virginia* (Norton, New York, 1975).
12. D. B. Quinn, *Set Fair for Roanoke* (Univ. of North Carolina Press, Chapel Hill, 1985).
13. D. Stick, *Roanoke Island, The Beginnings of English America* (Univ. of North Carolina Press, Chapel Hill, 1983).
14. C. Earle, in *The Chesapeake in the Seventeenth Century: Essays on Anglo-American Society*, T. W. Tate and D. L. Ammerman, Eds. (Univ. of North Carolina Press, Chapel Hill, 1979), pp. 96–125.
15. I. N. Hume, *The Virginia Adventure* (Knopf, New York, 1994), p. 132.
16. B. J. Prugh, P. E. Herman, D. L. Belval, *Water-Data Report VA-91-1* (U.S. Geological Survey, Richmond, VA, 1992).
17. We thank G. M. Williamson, T. P. Harlan, and J. Young; the landowners B. Phillips and J. F. Johnson III; and the Kirk Lumber Company for assisting the protection of the ancient baldcypress trees on the Pompeii Tract at Blackwater River. Supported by the National Science Foundation, Paleoclimatology Program (grant ATM-9528148), and The College of William and Mary, Williamsburg, VA, with support from the National Park Service. The observed and reconstructed July PHDI may be obtained from the National Geophysical Data Center at ftp://ftp.ngdc.noaa.gov/paleo/treering/reconstructions/jamestown-roanoke/

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Tunneling into a Single Magnetic Atom: Spectroscopic Evidence of the Kondo Resonance

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The Kondo effect arises from the quantum mechanical interplay between the electrons of a host metal and a magnetic impurity and is predicted to result in local charge and spin variations around the magnetic impurity. A cryogenic scanning tunneling microscope was used to spatially resolve the electronic properties of individual magnetic atoms displaying the Kondo effect. Spectroscopic measurements performed on individual cobalt atoms on the surface of gold show an energetically narrow feature that is identified as the Kondo resonance—the predicted response of a Kondo impurity. Unexpected structure in the Kondo resonance is shown to arise from quantum mechanical interference between the *d* orbital and conduction electron channels for an electron tunneling into a magnetic atom in a metallic host.

The smallest magnetic structure in condensed matter physics is a single magnetic atom in a nonmagnetic host, often referred to as a Kondo impurity. The spin of a Kondo impurity interacts with the spin of surrounding conduction electrons, leading to anomalous transport properties in dilute magnetic alloys (the Kondo effect) (*1*). For temperatures below a characteristic Kondo temperature (T_K), this interaction causes the electrons of the host metal to condense into a many-body ground state that collectively screens the local spin of the Kondo impurity (*2*). This screening cloud exhibits a dense set of low-energy excitations called the Kondo resonance that strongly influence Kondo systems (*2*, *3*). Hallmarks of the Kondo effect are the disappearance of the Kondo resonance at temperatures above T_K, and the splitting of the resonance in an applied magnetic field (*2*). Although this theoretical picture has developed over more than 30 years and explains a wealth of data on magnetic alloys and rare earth compounds (*2*, *4*), there remains a surprising lack of direct experimental confirmation of the theory. For example, to date there has been no direct spectroscopic observation of the Kondo resonance for an isolated, well-characterized magnetic impurity in a nonmagnetic host (*5*), nor have there been conclusive measurements of the size of the Kondo screening cloud (*6*–*8*).

We report measurements of the local electronic structure of an isolated Kondo impurity on a metallic substrate. We used a scanning tunneling microscope (STM) to obtain spectroscopic data on individual cobalt (Co) atoms deposited onto the (111) face of a clean gold (Au) crystal at 4 K. These measurements reveal an electronic resonance centered about the Fermi energy (E_F) that has an energy width of only 11 meV and is localized to within a radius of 10 Å from the center of a Co atom. Because Co-Au is a known Kondo system (*3*, *9*–*11*), we interpret these data as evidence of the Kondo resonance for a single, well-characterized magnetic impurity. The line shape of the observed Kondo resonance is not Lorentzian, but rather has the asymmetric shape that is characteristic of a Fano resonance (*12*). We can explain this line shape by generalizing Fano's formalism to include tunneling into an impurity with strong Coulomb repulsion. Asymmetry in the Kondo resonance line shape is thus understood to result from quantum interference between the *d* orbital and continuum tunneling channels of the magnetic atom.

Cobalt in bulk Au has a high Kondo temperature (300 to 700 K) (*3*, *9*, *10*), and there is evidence that Co atoms are magnetic on Au surfaces with T_K = 19 K (*11*). At 4 K the collective Kondo ground state is thus formed ($T < T_K$). We cleaned the single crystal Au(111) substrate in ultrahigh vacuum (UHV) by repeated cycles of Ar ion sputtering and annealing. The Au(111) surface was then cooled to 4 K and dosed in UHV with a calibrated Co evaporator. Imaging and spectroscopy were performed with a homemade UHV STM held at the same temperature as the Au sample (4 K). The convention used here is that the bias across the STM tunnel junction (V) is the voltage of the sample with respect to the tip.

A 400 Å by 400 Å image of the Au(111) surface after deposition of a 0.001 monolayer coverage of Co (Fig. 1) shows the well-known Au(111) herringbone reconstruction (*13*), seen as ridges (or "soliton walls") traversing the surface. The soliton walls separate regions of face-centered cubic (fcc) and hexagonal close-packed (hcp) ordering on the surface (*13*). Approximately 22 well-isolated Co atoms can be seen as regular 0.8 Å high cones scattered about the surface (some surface defects can also be seen). Closer examination shows that the Au sur-

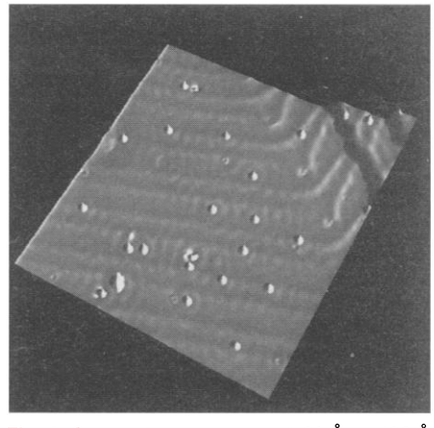

Fig. 1. Constant-current image (400 Å by 400 Å) of the Au(111) surface after deposition of 0.001 monolayer of Co at 4 K (tunnel parameters: I = 0.5 nA, V = 0.1 V). Approximately 22 Co atoms can be seen nestled among the ridges of the Au(111) herringbone reconstruction.

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face is decorated by low-amplitude waves. These arise from the quantum interference of two-dimensional surface-state electrons that exist on Au(111) (*14*). The Co atoms induce circular waves (Friedel oscillations) in the surface-state density, as do other nonmagnetic atoms and defects (*15*, *16*).

We performed STM spectroscopy at the site of individual Co atoms by measuring the bias dependence of the differential conductance, $dI/dV(V)$, of the STM tunnel junction. For $V > 0$ this quantity gives a measure of the rate of electronic transitions from the states at E_F on the tip to the states at $E_F + eV$ on the surface (*17*). This can be interpreted as a measure of the density of electronlike excitations of the surface having energy eV measured with respect to E_F ($V < 0$ samples holelike excitations). By changing the location of the tip it is possible to measure the spatial profile of these states, or excitations. dI/dV spectra of the Co/Au surface were measured through lock-in detection of the ac tunnel current driven by a 450-Hz, 1-mV (root-mean-square) signal added to the junction bias.

Figure 2 shows dI/dV spectra measured on and off of a single Co atom on the Au(111) surface. We measured the spectra by fixing the tip-surface separation to a value corresponding to a tunnel junction resistance of 2×10^8 ohm, and then sweeping the bias with the STM feedback loop opened. The top solid curve shows the dI/dV spectrum measured with the tip held over the bare Au surface, laterally displaced 12 Å away from a Co atom. The bare Au spectrum is relatively flat away from a Co atom. The bottom solid curve shows the dI/dV spectrum measured with the STM tip held over the center of a single Co atom lying between two soliton walls on the surface. Here the spectrum shows a strong, asymmetric resonance around $V = 0$, revealing sharp structure in the low-energy excitation spectrum of the surface near a Co atom. This feature was observed for hundreds of different Co atoms with a variety of different tips (*18*). We measured the tip-height dependence of the Co resonance by obtaining dI/dV spectra after fixing the tip-surface separation to values corresponding to resistances of 2×10^7 and 2×10^6 ohm. No significant change in the resonance line shape was observed over this range of separations, showing the resonance to be relatively insensitive to tip-surface separation.

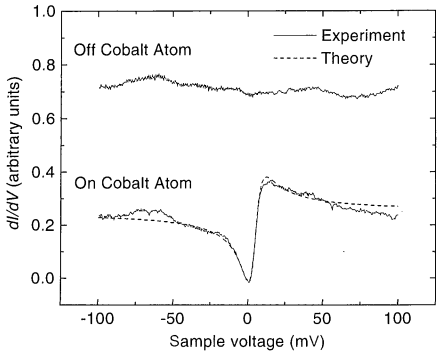

Fig. 2. A pair of dI/dV spectra taken with the STM tip held over a single Co atom and over the nearby bare Au surface (a constant slope has been subtracted from both curves, and they have been shifted vertically). The feature identified as a Kondo resonance appears over the Co atom (the ratio of the amplitude of the resonance feature to the overall conductivity is 0.3). Dashed curve shows a fit to the data with a modified Fano theory (Eqs. 1 to 3 in the text).

The resonance line shape also appears insensitive to the proximity of other Co atoms for interatom spacings down to 6 Å and to whether an atom is lying in an hcp or fcc region of the herringbone reconstruction. Atoms lying directly on the soliton walls, however, exhibit a slightly different resonance line shape that is greatly reduced in amplitude compared to atoms lying in either the hcp or fcc regions of the surface. Spectroscopic measurements of nonmagnetic copper atoms deposited on Au(111) did not show a resonance feature at E_F.

We measured the spatial dependence of the electronic structure of a single Co atom by acquiring dI/dV spectra with the STM tip held at varying distances from the center of an atom. As shown in Fig. 3, the resonance feature both decreases in amplitude and changes shape as the STM tip is moved outward from an atom's center. The resonance is mostly gone by a distance of 10 Å from the center of the atom. The resonance line shape tends to become more symmetric as the tip is moved radially outward. At a distance of −4 Å from the center of the atom, for example, the dI/dV spectrum shows a symmetric dip centered about $V = 0$ (*19*). Similar behavior was seen for other Co atoms.

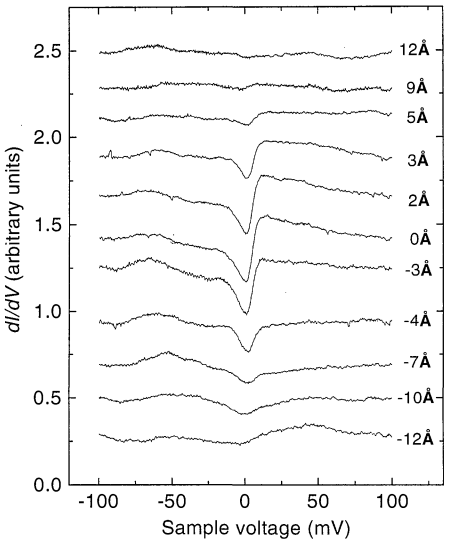

Fig. 3. A series of dI/dV spectra taken with the STM tip held at various lateral spacings from the center of a single Co atom on Au(111). (These data are from the same atom as the data shown in Fig. 2. A constant slope has been subtracted from each curve and they have been shifted vertically.)

To interpret tunneling spectroscopy of individual Co atoms, one must consider the excitation spectrum that is predicted for a magnetic atom upon the addition ($V > 0$) or subtraction ($V < 0$) of an electron. One powerful approach to this topic is the Anderson model of a magnetic impurity (*20*). With the Anderson model, a Co atom on Au can be thought of as a discrete d orbital in resonance with the continuum of Au conduction-band states. The d orbital is an interacting level; the energy associated with an occupancy of one electron is ε_d, whereas the energy to add a second electron is $\varepsilon_d + U$, where U represents the Coulomb interaction between two electrons in the d orbital ($U = 0$ for a noninteracting level). For a Co atom to be magnetic, $\varepsilon_d < E_F$ and $\varepsilon_d + U > E_F$ (*20*). The Anderson model has been well studied and is one of the simplest condensed-matter idealizations of a system of interacting electrons. As might be expected, the d orbital in this model spreads into a relatively broad d resonance that lies below E_F (the "bare" d resonance) (*20*). Less transparent, however, is the theoretical result that for temperatures below T_K, some of the d-orbital spectral density is shifted to E_F, forming a narrow, nearly Lorentzian resonance there (*2*). This is the many-body Kondo resonance, and the width of the resonance, ΔE, is proportional to the Kondo temperature, $\Delta E \propto k_B T_K$ (*2*), where k_B is the Boltzmann constant. For a tunneling experiment into the Kondo resonance, one might expect dI/dV to reflect this d-orbital spectral density and yield a Lorentzian-like peak about E_F [much photoemission data have been interpreted along these lines (*4*)]. Such an interpretation, however, assumes that electrons can only tunnel into the d orbital of a magnetic impurity and ignores electron tunneling into the surrounding continuum of conduction-band states. An electron tunneling from an STM tip to the Kondo resonance actually has two possible channels (the d orbital and the continuum) and this leads to an additional quantum interference term.

Fano has calculated the effect of such interference for transitions from an arbitrary initial state to a noninteracting discrete state in resonance with a continuum (that is, the $U = 0$ case of the Anderson model) (*12*). He has shown that the rate of transitions to a final state at energy ε can be expressed as

$$R(\varepsilon) = R_0(\varepsilon)\frac{(q + \varepsilon')^2}{1 + \varepsilon'^2}, \quad \varepsilon' = \frac{\varepsilon - \varepsilon_0}{\Gamma/2} \tag{1}$$

Here ε_0 is the energy of the discrete state, Γ is the width of the resonance, $R_0(\varepsilon)$ is the transition rate as it would be in the absence of the discrete state, and q is the ratio of the matrix elements linking the initial state to the discrete and continuum parts of the final state. We find that Fano's result can be generalized to an interacting resonant level (for $U \neq 0$) (*21*). The transition rate is still described by Eq. 1, but the energy parameter ε' is now given by

$$\varepsilon' = \frac{\varepsilon - \varepsilon_0 - Re[\Sigma(\varepsilon)]}{\mathrm{Im}[\Sigma(\varepsilon)]} \tag{2}$$

Here $\Sigma(\varepsilon)$ is the full self-energy of the resonant level including both interactions and coupling to the continuum. In the noninteracting case, of course, Eq. 2 simply reproduces Fano's results. With interactions, both the real and imaginary parts of the self-energy may be complicated functions of ε. However, near the Kondo resonance at E_F (for temperatures less than T_K), one finds (*22*)

$$Im[\Sigma(\varepsilon)] = \Gamma/2,$$
$$\varepsilon - \varepsilon_0 - Re[\Sigma(\varepsilon)] = \frac{(\varepsilon - \alpha)\Gamma}{2k_BT_K} \tag{3}$$

so that the simple Fano line shape continues to apply but with an overall width given by $\Delta E = 2k_BT_K$ (Γ is the width of the bare d resonance and α is a constant). The dashed curve in Fig. 2 shows a fit of Eqs. 1 to 3 to the spectrum obtained while the STM tip is held over the center of a Co atom. An excellent fit is obtained for the values $k_BT_K = 5.5$ meV, $\alpha = 4.5$ meV, and $q = 0.7$. Measurements taken on nine different Co atoms with four different tips (*18*) yield the average values $k_BT_K = 5.8 \pm 0.7$ meV, $\alpha = 6.5 \pm 1.3$ meV, and $q = 0.6 \pm 0.1$ (the parameters vary slightly depending on the condition of the tip and the position of the atom on the surface).

The fit to Eq. 1 reveals that the Kondo temperature for a Co atom on Au(111) is 70 K, confirming that the measurements were made in the $T < T_K$ limit. This value of T_K is much lower than values quoted for Co impurities in bulk Au, which range from 300 to 700 K (*3*, *9*, *10*). The lower surface T_K value is not surprising because Co impurities in the bulk have more neighboring atoms, thus increasing the overlap of the d orbital with conduction-band states and leading to a wider Kondo resonance. The value obtained here for surface T_K is, however, somewhat greater than the value of 19 K measured for Co on Au through use of a weak localization-based technique (*11*). One possible reason for the discrepancy is that Co was deposited onto disordered films for the weak localization measurements, as opposed to the oriented crystal used here.

An alternative explanation for the resonance shown in Fig. 2 is that it is not a Kondo resonance but is due to tunneling into a "bare" d resonance that happens to lie at E_F. We believe that this is not the case for two reasons. (i) Photoemission results imply that the 3*d* state of Co deposited onto Au(111) does not lie right at E_F, but rather 0.8 eV below it (*23*). (ii) The width of the resonance observed here (only 11 meV) is much narrower than the typical width of a bare d resonance. A d resonance usually measures hundreds of millielectron volts in width (*3*, *24*–*26*) [even for an adsorbate (*17*, *27*)], whereas the Kondo resonance, a collective effect, is expected to have a much narrower width (on the order of k_BT_K).

The spatial dependence of the dI/dV spectra measured across a single Co atom shows that the asymmetry parameter, q, decreases as the tip moves outward from the center of an atom. At a position of −4 Å (below center), q has decreased from the maximum central value of $q = 0.7$ to a value of only $q = 0.1$. This can be interpreted as meaning that the tunnel matrix element connecting the STM tip to the d-orbital channel decreases as the tip moves away from the atom's center, whereas the matrix element connecting the tip to the continuum channel stays roughly constant. The spatial dependence of the line shape asymmetry thus reflects the spatial extent of the Co d orbital. The overall decrease in the amplitude of the resonance as the tip moves even further out is likely due to increased coupling of the STM tip to continuum states with higher angular momentum (about the impurity) that do not couple to the d orbital.

In conclusion, a narrow spectroscopic feature associated with individual Co atoms on Au is identified as the Kondo resonance in the low-temperature limit ($T < T_K$). The asymmetric line shape of this feature is understood as a Fano resonance for an interacting discrete state coupled to a continuum. To further characterize the resonance it would be useful to perform similar spectroscopic measurements at higher temperatures, as well as in an applied magnetic field. At temperatures above T_K, for example, the Kondo resonance is predicted to disappear, while a magnetic field should split the resonance by the Zeeman energy (*2*). Such measurements open up new possibilities for probing magnetic nanostructures with the STM.

Note added in proof: Since the submission of this manuscript, we have become aware of a similar observation for Ce atoms on Ag(111) (*28*).

REFERENCES AND NOTES

1. J. Kondo, *Prog. Theor. Phys.* **32**, 37 (1964).
2. A. C. Hewson, *The Kondo Problem to Heavy Fermions* (Cambridge Univ. Press, Cambridge, 1993).
3. G. Grüner and A. Zawadowski, *Rep. Prog. Phys.* **37**, 1497 (1974).
4. J. W. Allen, in *Synchrotron Radiation Research: Advances in Surface and Interface Science*, R. Z. Bachrach, Ed. (Plenum, New York, 1992), vol. 1, pp. 253–323.
5. Spectroscopic features have been attributed to the Kondo resonance for systems other than a single, well-characterized magnetic impurity in a nonmagnetic host. See, for example, S. Gregory, *Phys. Rev. Lett.* **68**, 2070 (1992); D. C. Ralph and R. A. Buhrman, *ibid.* **72**, 3401 (1994); D. Goldhaber-Gordon *et al.*, *Nature* **391**, 156 (1998); E. L. Wolf, *Principles of Electron Tunneling Microscopy* (Oxford Univ. Press, New York, 1985). The pair-breaking effect of a single magnetic atom on a superconductor has also been observed [A. Yazdani, B. A. Jones, C. P. Lutz, M. F. Crommie, D. M. Eigler, *Science* **275**, 1767 (1997)].
6. J. B. Boyce and C. P. Slichter, *Phys. Rev. Lett.* **32**, 61 (1974).
7. V. Chandrasekhar *et al.*, *ibid.* **72**, 2053 (1994).
8. M. A. Blachly and N. Giordano, *Phys. Rev. B* **51**, 12537 (1995).
9. D. Riegel and K. D. Gross, *Physica B* **163**, 678 (1990).
10. M. D. Daybell and W. A. Steyert, *Rev. Mod. Phys.* **40**, 380 (1968).
11. W. Wei, R. Rosenbaum and G. Bergmann, *Phys. Rev. B* **39**, 4568 (1989).
12. U. Fano, *Phys. Rev.* **124**, 1866 (1961).
13. C. Wöll, S. Chiang, R. J. Wilson, P. H. Lippel, *Phys. Rev. B* **39**, 7988 (1988).
14. S. D. Kevan and R. H. Gaylord, *ibid.* **36**, 5809 (1987).
15. M. F. Crommie, C. P. Lutz, D. M. Eigler, *Nature* **363**, 524 (1993).
16. Ph. Avouris, I.-W. Lyo, R. E. Walkup, *J. Vac. Sci. Technol. B* **12**, 1447 (1994).
17. N. D. Lang, *Phys. Rev. B* **34**, 5947 (1986).
18. "Different tips" were obtained by changing the microscopic arrangement of the last few atoms on the STM tip through field emission and gentle collisions with the surface.
19. dI/dV traces taken with the tip displaced over the opposite side of the atom shown in Fig. 3 do not show as great a change in lineshape asymmetry. We attribute this to asymmetry in the particular STM tip used to acquire the data shown in Fig. 3.
20. P. W. Anderson, *Phys. Rev.* **124**, 41 (1961).
21. Previous analysis of tunneling into an Anderson impurity [Y. Meir and N. S. Wingreen, *Phys. Rev. Lett.* **68**, 2512 (1992)] can be generalized straightforwardly to include tunneling into the continuum.
22. A. Houghton, N. Read, H. Won, *Phys. Rev. B* **35**, 5123 (1987).
23. R. Mamy and B. Carricaburu, *J. Phys. Cond. Matter* **5**, 6537 (1993).
24. H. S. Reehal and P. T. Andrews, *J. Phys. F Metal Phys.* **10**, 1631 (1980).
25. P. Steiner, H. Hochst, W. Steffen, S. Hufner, *Z. Physik B* **38**, 191 (1980).
26. R. Podloucky, R. Zeller, P. H. Dederichs, *Phys. Rev. B* **22**, 5777 (1980).
27. N. D. Lang, *Phys. Rev. Lett.* **58**, 45 (1987).
28. J. Li, W.-D. Schneider, R. Berndt, B. Delley, unpublished results.

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