Kondo Scattering Observed at a Single Magnetic Impurity

Jiutao Li* and Wolf-Dieter Schneider†
Institut de Physique Expérimentale, Université de Lausanne, CH-1015 Lausanne, Switzerland

Richard Berndt
2. Physikalisches Institut, Rheinisch-Westfälische Technische Hochschule Aachen, D-52056 Aachen, Germany

Bernard Delley
Paul Scherrer Institut, CH-5232 Villigen, Switzerland

(Received 6 October 1997)

Electron scattering of isolated Ce adatoms on Ag(111) surfaces was studied with a low-temperature scanning tunneling microscope. Tunneling spectra obtained on and near Ce reveal a characteristic dip around the Fermi energy which is absent for nonmagnetic Ag adatoms. This feature is detected over a few atomic diameters around Ce atoms at the surface. The transition matrix element from the localized f electron to the tunnel-current carrying continuum states bears a strong resemblance to discrete autoionized states. We interpret the dip spectrum as a Fano interference for the limit where the f orbital has a very small matrix element. [S0031-9007(98)05691-9]

PACS numbers: 72.15.Qm, 61.16.Ch, 72.10.Fk

Scattering of conduction electrons at a magnetic impurity gives rise to unconventional phenomena in magnetism, transport properties, and the specific heat which have been successfully described within the Anderson single impurity model (SIM) [1]. These peculiar properties result from the interplay between well localized d or f electrons and the tendency to delocalization provoked by hybridization with band electrons. In the Kondo picture, for rare earth systems, the local $4f$ moment is gradually screened as the temperature approaches $T = 0$ K and a many-body nonmagnetic singlet ground state is formed around the Fermi energy [2]. These low-energy excitations, termed Kondo resonance with a characteristic width of $\delta = kT_{\mathrm{K}}$ (T_{K} is the Kondo temperature and k the Boltzmann constant) have been directly observed for a number of homogeneous dense Kondo compounds using high-resolution photoelectron spectroscopy [3–5] which averages over a typical surface area of 1 mm^2.

However, no direct measurement has been reported so far which reveals the manifestations of the Kondo effect on an atomic length scale on and around a single magnetic impurity. We directly probed the scattering of Ag(111) surface state electrons in the vicinity of a single Ce impurity with a low-temperature scanning tunneling microscope (STM). In the tunneling spectra an antiresonance occurs when the tip is placed on top of a Ce adatom. Using the SIM we interpret this antiresonance in the tunneling spectra in terms of a Fano interference phenomenon. Figuratively speaking, this antiresonance may be termed a "footprint" of the Kondo resonance observed in photoemission.

Previously and relevant for the present investigation, the STM has been used to perform local spectroscopy with atomic scale resolution in a study of Fe atoms on a clean Pt(111) surface [6]. Resonances of 0.5 eV width were found in the adatom local density of states (LDOS) above the Fermi level. Later on, characteristic standing wave patterns around single adatoms have been observed in spatially resolved spectroscopic STM images [7–9]. Recently the local effects of isolated magnetic impurities on the electronic properties of a classical superconductor were studied with scanning tunneling spectroscopy (STS) [10]. Here we report on the effects of magnetic and nonmagnetic adatoms on the LDOS on Ag(111). In particular, we interpret a depletion of the LDOS near the Fermi energy which occurs for Ce only in terms of Kondo scattering.

The experiments were performed with a homebuilt ultrahigh vacuum (UHV) low-temperature STM [11]. The Ag(111) surface was prepared by Ar ion bombardment and annealing cycles. Isolated Ce atoms and, for comparison, isolated Ag atoms on Ag(111) were deposited by evaporation from a tungsten filament onto the Ag substrate held at $T = 5$ K. Upon deposition at $T = 50$ K Ce cluster formation is observed [12]. After dosing the surface with one kind of impurity, the surface was imaged to detect the isolated adatoms on the Ag(111) terraces. The adatoms appear as protrusions with ≈0.9 Å and ≈1.2 Å height for Ag and Ce, respectively, with typical widths of ≈15 Å in constant current topographs taken at a tunneling resistance of a few hundred MΩ [12]. A measure of the LDOS of the Ag(111) surface was obtained from measurements of the differential conductance dI/dV versus the sample bias voltage V performed under open feedback loop conditions with lock-in detection (243 Hz, 2–4 mV$_{\mathrm{rms}}$ sinusoidal modulation added to the bias). These tunneling spectra were measured using three electrochemically etched W tips which were prepared in UHV by heating and Ar ion bombardment. Each of these tips was repeatedly and intentionally modified by applying voltage pulses and by bringing it into contact with the Ag surface. The spectroscopic features discussed below were observed with all these tips over a range of tip-sample distances defined by the tunneling parameters (500 mV $> V >$ −500 mV, 100 pA $< I <$ 2 nA) used prior to opening the feedback loop.

Ce impurity atoms have been chosen because of their known magnetic behavior in bulk Ce compounds [4] and their high T_K (≈1000 K in α-Ce [1,5]). For comparison, Ag as a prototype for a nonmagnetic atom was also investigated. The effect of these adsorbed impurities on the Ag(111) surface state electrons was studied locally by STS. Spectra of dI/dV were taken for varying lateral distances from Ag and Ce adatoms. Figure 1 displays typical results of such measurements. Spectra taken on top of a Ag adatom [Fig. 1(a)] are featureless over an energy range from −300 to 300 mV. These spectra change gradually with increasing lateral distance from the Ag adatom [Figs. 1(b)–1(d)] until finally [Fig. 1(e)] the characteristic onset of the Ag(111) surface state at ≈−70 mV is observed [8,9]. We note that due to lattice contraction the surface state onset at $T = 5$ K is located at ≈−70 mV in agreement with photoelectron spectroscopy data [13]. We note that spectra taken at monatomic steps of Ag(111) closely resemble the one in Fig. 1(a).

By contrast, the scattering of the Ag(111) surface state electrons at Ce is distinctly different (Fig. 2). The dI/dV spectrum measured on top of a Ce adatom [Fig. 2(a)] displays a gaplike feature around the Fermi energy. With increasing lateral distance of the tip from the Ce impurity atom the onset of the Ag(111) surface state becomes discernible [Figs. 2(b)–2(d)]. The surface state edge appears broadened and shifted to higher energies with respect to the edge observed on a large terrace. Only at a distance of about 40 Å from the Ce adatom [Fig. 2(g)] the spectrum becomes nearly identical to the one obtained on a clean Ag(111) terrace. (The weak spectral features above the onset of the surface state are due to standing wave patterns caused by scattering at the adatoms [7,8,14].) We repeated these measurements on Ce clusters and on thin Ce films at $T = 50$ K. As shown in Fig. 3 the characteristic dip around the Fermi level which is distinct from the situation encountered on top of Ag atoms is always observed. Its width, however, increases from about 50 mV on top of the Ce to about 100 mV on a Ce film [12].

In order to rationalize the spectroscopic characteristics observed in the present experiments a model calculation within the Anderson SIM for a single magnetic $4f$ impurity embedded in a bulk conductor was performed. This type of many-body calculation has already been applied successfully to photoemission spectra of heavy fermion systems [4,5] and transition metal surface alloys [15]. To a first approximation, due to an enhanced $4f$ electron ionization cross section at higher photon energies (above 30 eV) with respect to sp band electrons, photoemission yields predominantly the $4f$ spectral function including the low energy excitations, i.e., the Kondo resonance

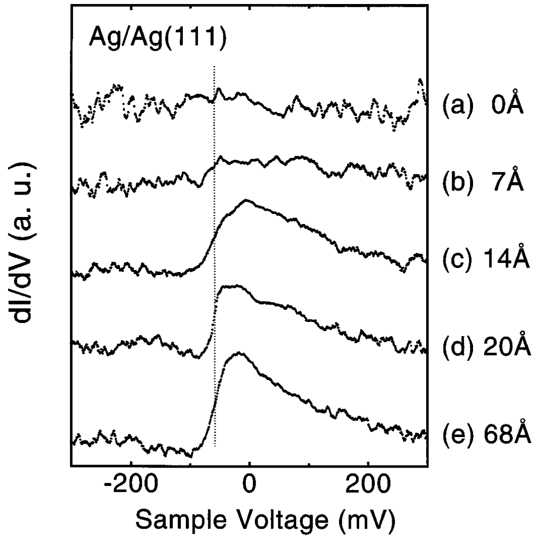

FIG. 1. Differential conductance (dI/dV) spectra on and near a single Ag adatom at $T = 5$ K. The lateral distance between the tip position and the center of the Ag adatom is indicated. The dashed line marks the onset of the Ag(111) surface state. Tunneling parameters prior to opening the feedback loop $V = -500$ mV, $I = 0.2$ nA.

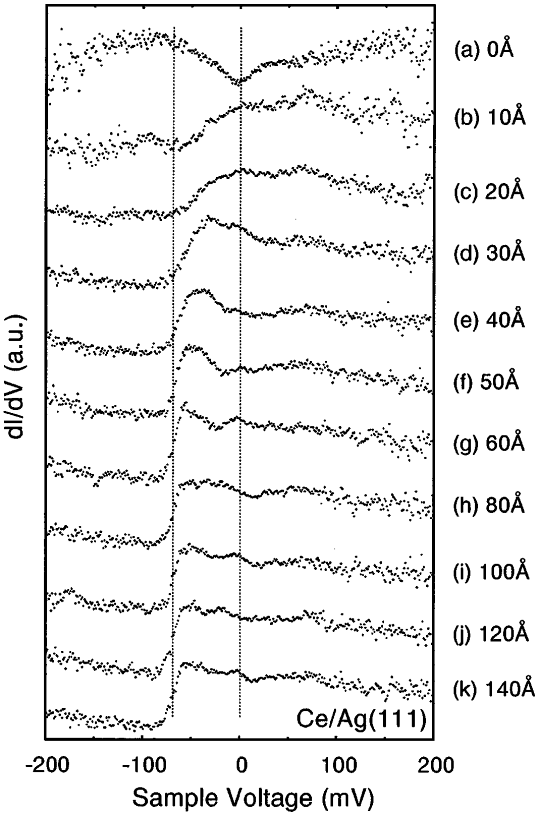

FIG. 2. dI/dV spectra on and near a single Ce adatom at $T = 5$ K. The lateral distance between the tip position and the center of the Ce adatom is indicated. The vertical dashed lines at −70 and 0 mV mark the onset of the Ag(111) surface state and the Fermi energy. Before opening the feedback loop the tunnel parameters were $V = 200$ mV, $I = 0.1$ nA.

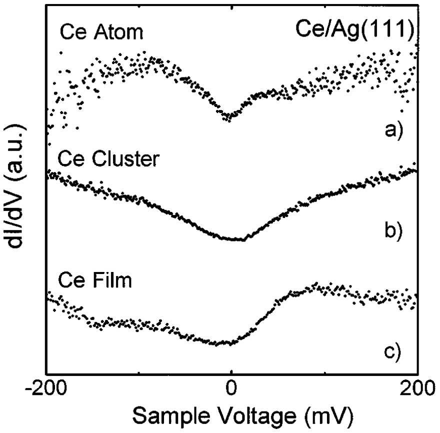

FIG. 3. dI/dV spectra (a) on a single Ce adatom at $T = 5$ K, (b) on a Ce cluster at $T = 50$ K, and (c) on a Ce film of more than 10 monolayer thickness at $T = 50$ K. Tunneling parameters prior to opening the feedback: (a) $V = 200$ mV, $I = 0.1$ nA, (b) $V = 500$ mV, $I = 1$ nA, (c) $V = 350$ mV, $I = 1$ nA.

around the Fermi level [2]. By contrast, the STM—at the tip adatom distances used in the present experiment—probes sp wave functions rather than the confined $4f$ wave function [16]. Thus, due to hybridization between the localized $4f$ state and the extended conduction band states STM should be locally sensitive to the hybridized sp conduction band.

We observe that the probing of a localized state immersed in a continuum by the tunneling microscope bears a resemblance to the spectroscopy of a discrete autoionized state, which has been theoretically elucidated by Fano [17]. In the limit where the transition matrix element for the localized state approaches zero ($q \approx 0$ case in Ref. [17]), the autoionization spectrum shows a dip or antiresonance, as a consequence of the interference effects at the site with the localized state. The width of the antiresonance is on the same scale as that of the resonance. In the case of the STM probe, the matrix element to the localized $4f$ function should be very small by the argument of Lang [16], and the spectrum should show antiresonances instead of f-spectral peaks. It is a peculiarity of the low temperature singlet ground state of magnetic impurities to always show a sharp "Kondo" resonance for the localized function at the Fermi energy. Such f spectra for Ce compounds have been calculated by various approaches: the zero temperature Gunnarsson-Schönhammer theory [2] and the slave boson approach [18,19]. We have applied these types of theories and shown that for reasonable parameters Kondo peaks of the scale observed here as antiresonance do appear. Specifically, we performed calculations of the f density of states within the noncrossing approximation (NCA) [18,19] at $kT = 1$ meV, with parameters for the bare $4f$ energy (-1.2 eV), $4f$ spin orbit splitting (280 meV), crystal field splitting neglected and the $4f$ conduction band hybridization (60 meV) in the range of published values for CeAg alloys [20]. Since the difference between a calculation for an embedded versus an adsorbed impurity is reflected only in the NCA coupling strength this many-body approach is applicable in the present case yielding the narrow Kondo f resonance known from photoemission. From the Fano argument of the interference between the two channels it follows that there exists a symmetric dip with zero transmission at the center energy (0 mV) with the same width as the f resonance. Since there may be other symmetry channels which add nondip related transmission and since the finite instrumental resolution is masking finer details of the line shape we have approximated the NCA-Fano dip shape by the inverse NCA line shape. The dip depth is a pure fit parameter. In order to account for lifetime and instrumental (modulation) influences a Gaussian broadening of 16 meV was applied [12]. (For the present purpose we ignore further details of the tunneling process such as the variation of the tunneling probability over the limited energy range.) The result, shown by the solid curve in Fig. 4, reveals an encouraging agreement with the experimental observations (full squares). The calculated width of the Kondo peak $\delta \approx 50$ meV corresponds well to the experimentally observed width of the dip around the Fermi level in the tunnel spectra. The small asymmetry observed in the experimental spectrum with respect to the Fermi energy can be interpreted as a manifestation of the Fano-interference effect which occurs when there is a small transmission probability to/from f symmetry states. The observed increase of the width of the dip on Ce clusters and Ce films as compared to the single Ce atom is expected within the SIM and is consistent with the increase in hybridization due to overlap between neighboring Ce atoms.

Thus we conclude that the Kondo resonance observed in photoemission appears as a Kondo antiresonance in the tunneling spectra. In other words, the Kondo resonance in STS manifests itself by reducing the differential conductance for tunneling transmission near the Fermi level because of destructive interference between transitions into localized and delocalized orbitals near the resonance. This effect has not been considered in an earlier theoretical

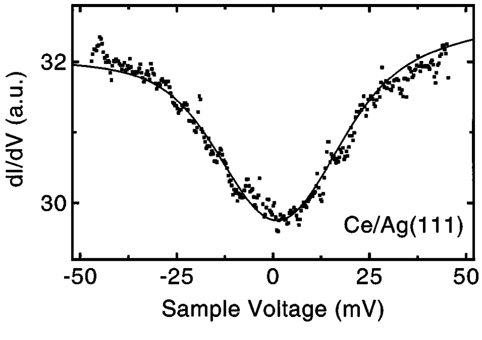

FIG. 4. dI/dV spectra of a Ce impurity on Ag(111) for an energy range around the Fermi level. Squares: measurement ($V = 100$ mV, $I = 0.1$ nA before opening the feedback loop). Solid line: Calculation (see text).

prediction of probing the Kondo resonance by resonant tunneling through an Anderson impurity [21]. Moreover, we note in passing that the reappearance of the surface state onset in the tunneling spectra at a lateral distance of about 40 Å from the magnetic impurity may indicate the lateral influence of Kondo scattering on a quasi-two-dimensional system at low temperature.

While the present study is the first step towards an understanding of magnetic impurity scattering at an atomic level this work may be extended to impurities which are embedded within the first atomic surface layer. In such systems, where no impurity diffusion is expected in the temperature range of the collapse of the Kondo resonance, the influence of temperature on the shape of the antiresonance may be observable.

We acknowledge fruitful discussions with F. Patthey and the financial support of the Swiss National Science Foundation.

Note added.—After the original submission of this manuscript we have become aware of a similar observation for Co atoms on Au(111) by Madhaven *et al.* [22].

---

*Present address: Beckman Institute, Department of Electrical and Computer Engineering, University of Illinois at Urbana-Champaign, Urbana-Champaign, IL.

†Presently on a sabbatical leave at the Department of Physics and Astronomy, University of Hawaii at Manoa, Honolulu, HI 96822.

[1] P. A. Lee, T. M. Rice, J. W. Serene, L. S. Sham, and J. W. Wilkins, Comments Condens. Matter Phys. **12**, 99 (1986).

[2] O. Gunnarsson and K. Schönhammer, in *Handbook on the Physics and Chemistry of Rare Earths,* edited by K. A. Gschneidner, L. Eyring, and S. Hüfner (Elsevier Publisher, Amsterdam, 1987), Vol. 10, p. 103, and references therein.

[3] F. Patthey, J.-M. Imer, W.-D. Schneider, H. Beck, Y. Baer, and B. Delley, Phys. Rev. B **42**, 8864 (1990).

[4] D. Malterre, M. Grioni, and Y. Baer, Adv. Phys. **45**, 299 (1996).

[5] M. Garnier, K. Breuer, D. Purdie, M. Hengsberger, Y. Baer, and B. Delley, Phys. Rev. Lett. **78**, 4127 (1997).

[6] M. F. Crommie, C. P. Lutz, and D. M. Eigler, Phys. Rev. B **48**, 2851 (1993).

[7] M. F. Crommie, C. P. Lutz, and D. M. Eigler, Nature (London) **363**, 524 (1993); E. J. Heller, M. F. Crommie, C. P. Lutz, and D. M. Eigler, Nature (London) **369**, 464 (1994).

[8] Y. Hasegawa and Ph. Avouris, Phys. Rev. Lett. **71**, 1071 (1993); Ph. Avouris and I.-W. Lyo, Science **264**, 942 (1994).

[9] J. T. Li, W.-D. Schneider, and R. Berndt, Phys. Rev. B **56**, 7656 (1997).

[10] A. Yazdani, B. A. Jones, C. P. Lutz, M. F. Crommie, and D. M. Eigler, Science **275**, 1767 (1997).

[11] R. Gaisch, J. K. Gimzewski, B. Reihl, R. R. Schlittler, M. Tschudy, and W.-D. Schneider, Ultramicroscopy **42–44**, 1621 (1992).

[12] J. T. Li, Ph.D. thesis, University of Lausanne, Switzerland, 1997.

[13] R. Paniago, R. Matzdorf, G. Meister, and A. Goldmann, Surf. Sci. **336**, 113 (1995).

[14] J. T. Li, W.-D. Schneider, R. Berndt, and S. Crampin, Phys. Rev. Lett. (to be published).

[15] H.-V. Roy, J. Boschung, F. Patthey, P. Fayet, W.-D. Schneider, and B. Delley, Phys. Rev. Lett. **70**, 2653 (1993).

[16] N. D. Lang, Phys. Rev. Lett. **58**, 45 (1987).

[17] U. Fano, Phys. Rev. **124**, 1866 (1961).

[18] P. Coleman, Phys. Rev. B **29**, 3035 (1984).

[19] F. Patthey, W.-D. Schneider, Y. Baer, and B. Delley, Phys. Rev. Lett. **58**, 2810 (1987).

[20] P. Monachesi, L. C. Andreani, A. Continenza, and A. K. McMahan, J. Appl. Phys. **73**, 6634 (1993).

[21] S. Hershfield, J. H. Davies, and J. W. Wilkins, Phys. Rev. Lett. **67**, 3720 (1991).

[22] V. Madhaven, W. Chen, T. Jamneala, M. F. Crommie, and N. S. Wingreen, unpublished results.