

Observing the scattering phase shift of isolated Kondo impurities at surfaces

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The spin-flip scattering at Co adatoms on Ag(111) leads to the formation of a Kondo resonance. We determined the energy-dependent scattering phase shift of electrons scattering off single magnetic adatoms. A scanning tunneling microscope operating at 6 K was used to determine the amplitude of the Friedel oscillations created in the local density of states of the Ag(111) surface state electrons by the Co adatoms. We find that the standing-wave pattern around Co adsorbates exhibits a minimum in amplitude near E_F of width $2k_B T_K$, where $T_K=92$ K is the Kondo temperature of the system. The wave pattern amplitude as a function of energy can be explained by assuming an energy-dependent phase shift for the scattering process.

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The observation that magnetic impurities in a nonmagnetic host metal have a distinct influence on the scattering of the host metal electrons was recognized experimentally and theoretically long ago and is known as the Kondo effect. The nature of this scattering process includes the spin degree of freedom which is absent in other potential scatterers. Interest in the experimental investigation of single impurity Kondo systems was refocused, when it was shown that the Kondo resonance can be probed locally by scanning tunneling microscopy (STM). This was achieved for the case of Ce on Ag(111) (Ref. 1) and Co atoms adsorbed on Au(111) (Ref. 2) and Cu(111).³ All these substrates have a surface state at the Fermi level which has a parabolic free-electron-like dispersion and acts like a two-dimensional electron gas (2DEG). In the differential conductance spectra (dI/dV) the Kondo resonance manifests itself as a sharp depression at the Fermi energy with a characteristic Fano line shape. The occurrence of this line shape was successfully explained by theory, and results from the specific form of the local density of states (LDOS) of the conduction electrons,⁴ which is proportional to the measured dI/dV vs voltage curve, and (probably to a lesser extent) the relative importance of the two tunneling channels (through adsorbate and substrate states).⁵ Experimentally the resonance feature was visible only at the site of the impurity atom, whereas theory expected a long range variation of the observable line shape.^{4,5} Therefore the observation of Manoharan *et al.* came as a surprise that the Kondo dip [in the system Co on Cu(111)] could be observed 80 Å away from the Co atom sitting in one focus of an elliptical electron resonator by probing the other empty focus;³ this feature was called a “quantum mirage.”

Here we address an important aspect of the scattering process, namely, the phase imparted onto the electrons that scatter off the magnetic impurity. An energy-dependent phase shift was recently shown to explain the observed “quantum mirage” in elliptical resonators.⁶ We show that this phase shift can also be accurately determined with STM when the Co atoms are simply adsorbed on Ag(111) and are not explicitly placed in artificial resonators.

We used an Ag(111) single-crystal substrate, carefully prepared by sputtering and annealing cycles in UHV (base pressure in the low 10^{-10} mbar range). The resulting density of impurities visible in STM topographs was 3×10^{-5} ML.

After cleaning the sample was transferred *in situ* into a low-temperature STM attached to a He⁴ bath cryostat. Co was evaporated from a carefully cleaned 99.99% Co wire wound around a 99.95% W filament. The result after evaporation of 5×10^{-4} ML Co through an opening in the shield of the He cryostat is shown in Fig. 1. The temperature during evaporation was 18 K (which was determined by a dummy evaporation onto a temperature sensor installed instead of the sample). This procedure resulted in isolated Co atoms adsorbed on the Ag(111) surface. The density of other defects did not increase significantly. Subsequent measurements with the STM were done at 6 K; at that temperature the Co atoms are immobile. Spectroscopic measurements were performed using a lock-in technique with a modulation of the sample voltage of ~ 1 mV rms at a frequency of 2–4 kHz. All voltages are sample potentials measured with respect to the tip.

First we demonstrate that the isolated Co atom indeed forms a Kondo state on Ag(111). Figure 2 shows a representative dI/dV spectrum taken directly at the site of a Co adatom. Using different tips in the same way as in the experiments of Refs. 1–3 did not show significant changes of the line shape. The conduction vs voltage shows the characteris-

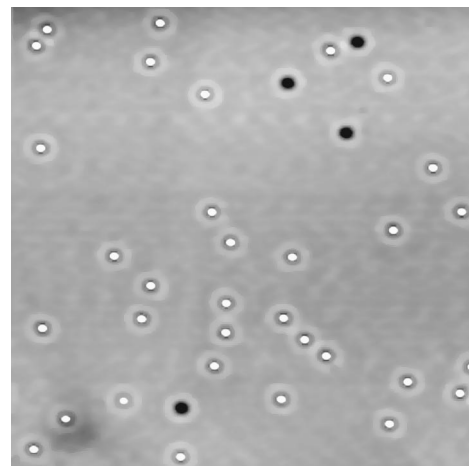


FIG. 1. STM topograph (62 nm^2) of the Ag(111) surface with deposited Co adatoms (bright) and residual impurities (dark) taken at a bias voltage of +200 mV.

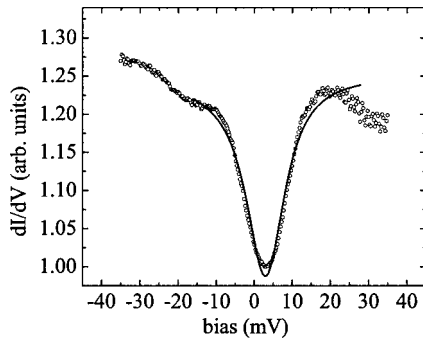


FIG. 2. Tunneling conductance spectrum taken on top of a Co atom adsorbed on Ag(111). The differential tunneling conductivity is normalized to the minimal value of the spectrum around E_F . Solid line: fit using the formula given in Ref. 4. The resulting Fano line-shape parameters are $q=0.0\pm 0.1$, Kondo temperature $T_K=92\pm 6$ K, and energy shift $\epsilon_K=3.1\pm 0.5$ meV.

tic Fano line shape around $E=E_F$.¹⁻³ We fitted data of 16 different adatoms using the model of Újsághy *et al.*⁴ and obtained a Kondo temperature of $T_K=92\pm 6$ K, a Fano parameter of $q=0.0\pm 0.1$, and a shift of the resonance to $\epsilon_K=3.1\pm 0.5$ meV above the Fermi level. The observed spectrum is only visible if the STM tip is positioned directly on the adatom; at a distance of 5 Å the amplitude of the observed dip has halved and is not measurable beyond 10 Å. We note that the spectrum shows the same symmetric line shape observed for Ce on Ag(111),¹ in contrast to the more asymmetric shapes found for Co on Au(111) (Ref. 2) and Cu(111).³ This is indicative of the prediction⁴ that the Fano q parameter is related to the electronic band structure of the host metal. In the following we will use other defects for normalization which we call “impurities” as a reference (Fig. 1). These defects remain on the surface after the cleaning process. We checked that they did not show a variation of the conductivity in the energy range discussed here, when probed with the same tip. We believe they are nonmagnetic adsorbates or surface defects originating from the bulk crystal.

Since the Kondo temperature is 92 K the experiments are done in the limit of $T\ll T_K$. In that limit scattering at the Kondo impurity can be mapped onto a scattering at a nonmagnetic impurity taking into account a special scattering phase shift which depends on energy (and electron density).⁸ From general scattering theory one would expect a scattering at the Kondo resonance which leads to a phase shift of π when sweeping the energy across the resonance level. To measure that phase shift we sought to detect it in the well-known interference pattern that an impurity produces in the LDOS of the 2DEG of the Ag(111) surface state, shown in Fig. 3(a). The most direct way to measure the phase shift of the scattered waves would be to measure this interference pattern for different energies and analyze the position of the maxima and minima of the waves. This suffers from the drawback that the lateral position of the extrema has to be determined very accurately. Since the interference pattern itself is mostly dominated by absorptive scattering the observable shift in position due to elastic scattering is very small.⁹ However, one can use the extreme vertical sensitivity of the

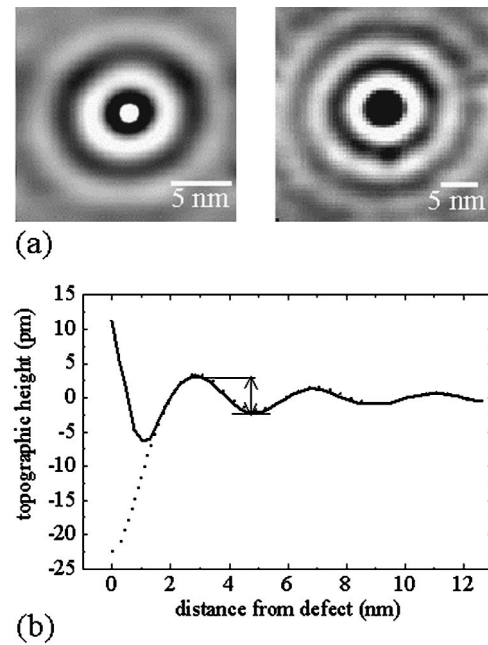


FIG. 3. (a) Interference pattern formed in the LDOS of the Ag(111) surface-state electrons at a Co adatom (left) and a nonmagnetic defect which we refer to as an “impurity” (right). (b) Definition of the wave amplitudes of the interference pattern Δz as indicated by an arrow. The quantity is extracted in a region ~ 4 nm away from the Co adatom (solid line) or impurity (dotted line).

STM to determine the amplitude of the scattered waves at the impurity using simply the topographic mode at different sample voltages. This kind of $z(V)$ spectroscopy was recently employed to study quantum states formed by subsurface defects.¹⁰ We define this amplitude Δz_{Co} to be the difference of z height between the first off-atom maximum and the second minimum [Fig. 3(b)]. With that definition we work in the far field of the scatterer on the clean Ag(111) terrace. The measured amplitude will first depend on voltage due to the fact that with higher voltages, electrons of different energies are taking part in the tunneling process thereby washing out the interference patterns. Second, it will depend on tip structure. It is well known that the “standing waves” become more or less intense with different atomic arrangements of the tip end. Therefore we normalized the measured amplitude at a Co atom by dividing it by the amplitude Δz_{imp} of the LDOS interference pattern measured at an impurity with the same tip (i.e., in the same image). We have checked that the impurities scatter the electrons with little variation in energy as does a step edge, which is known to act as a potential scatterer with little phase shift in the energy range studied.¹¹ We can therefore use the impurities as a reference of a purely potential scatterer imposed on the 2DEG of the surface state.

The wave amplitude at the cobalt adatoms normalized to that at the impurities is shown in Fig. 4. We find a minimum in the scattering intensity near E_F of width in energy comparable to $2k_B T_K$. The normalized wave amplitude shows a characteristic asymmetric line shape. We note that the absolute value of the reduced amplitude amounts to 5 pm com-

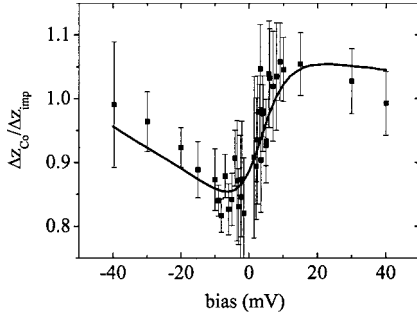


FIG. 4. Plot of the wave pattern amplitude around Co atoms normalized against the amplitude around impurities. The line is a model calculation assuming a resonant phase shift at the Fermi level with parameters $\delta_{bg} = -0.24\pi$, $\delta_{ab} = 0.97$, and $\delta_{ab}^{\text{imp}} = 2.1$ (see text).

pared to 6 pm as a “standard” wave amplitude, therefore most of the error is due to the finite stability of the instrument which is around 0.3 pm. Such a variation of the amplitude of the LDOS oscillations as a function of energy is not observed for other nonmagnetic scatterers. We therefore conclude that it is related to the interaction of the magnetic moment of the adsorbate with the surface-state electrons. To understand the dip in the wave amplitude at the Fermi level we calculated the quantity $\Delta z_{\text{Co}}/\Delta z_{\text{imp}}$ numerically. Writing the two-dimensional scattering T matrix as

$$T(E) = -\frac{1}{4\pi^2 L_0} e^{i\delta(E)} \sin \delta(E) \quad (1)$$

and using the standard expression for the system’s Green’s function,

$$G = G_0 + G_0 T G_0, \quad (2)$$

where G_0 is the unperturbed Green’s function of the surface-state electrons, we arrive at the LDOS around a Co adatom previously given by Heller *et al.*:⁹

$$\begin{aligned} \text{LDOS}(E, r) &= -\frac{1}{\pi} \text{Im}[G(r, r, E)] \\ &\approx_{kr>1} L_0 \left[1 + \frac{1}{2\pi^2} \text{Re} \left(\frac{e^{2i\delta} - 1}{2i} \frac{e^{2ikr}}{kr} \right) \right]. \quad (3) \end{aligned}$$

In this equation k is the energy-dependent wave vector of the surface-state electrons, L_0 is the LDOS of an unperturbed 2DEG with the effective mass of $0.4 m_e$, and δ is the s -wave phase shift of the electrons that are scattered at the defect, which in the case of the Kondo atom also becomes energy dependent (see below). In this model one takes δ to be a complex number, the imaginary part accounting for adsorption of the scattered wave. It is apparent that the lateral LDOS oscillations are minimal where the phase shift is zero. Equation (3) is valid in the far field of the scatterer, i.e., in the limit $kr > 1$.

The $z(V, r)$ trace was then calculated by integrating the LDOS to give the current (in the limit $T=0$ K):¹²

$$I(V, r) \propto \int_0^{eV} \text{LDOS}(E, r) dE. \quad (4)$$

$z(V, r)$ is then given by inverting the equation:

$$I_{sp} = e^{-2Az(V, r)} \times I(V, r), \quad (5)$$

where I_{sp} is the constant current setpoint, and A is the usual exponential prefactor containing the work function. To include the interaction with the Kondo state formed around the magnetic adatom, we follow a treatment by Újsághy *et al.*,⁴ where the Kondo physics is shown to produce at $T \ll T_K$ a narrow resonance in the d -orbital spectral function. From that an energy-dependent s -wave phase shift can be obtained for the electrons in the conduction band that has the form

$$\delta(E) = \frac{\pi}{2} + \tan^{-1} \left(\frac{E - \epsilon_K}{k_B T_K} \right) + \delta_{bg} + i \delta_{ab}. \quad (6)$$

This is the familiar form for scattering at a potential with a resonant level at $E = \epsilon_K$. This form was also used by Fiete *et al.*⁶ to analyze the “quantum mirages” in elliptical resonators.⁷ The energy-independent phase shift δ_{bg} is a parameter introduced to characterize the contribution from other scattering processes (e.g., d -band resonance). δ_{ab} introduces a loss of electrons due to absorptive scattering. Equations (3)–(6) were used to calculate the quantity $\Delta z_{\text{Co}}/\Delta z_{\text{imp}}$. For the LDOS around an impurity we assume a constant phase shift $\pi/2$, and fit the absorptive imaginary phase shift δ_{ab}^{imp} . This procedure is justified since the impurities act as highly absorptive point scatterers. An earlier experimental estimate was 0.37π ,¹³ using that value will change the obtained δ_{ab}^{imp} slightly within the error bounds. To reduce the number of free parameters we used the value for $k_B T_K = 8$ meV and $\epsilon_K = 3$ meV from the fit to the on-atom spectrum (Fig. 1). The role of the three parameters left is as follows: δ_{bg} controls the shape of the curve, δ_{ab} the depth of the minimum, and δ_{ab}^{imp} adjusts an offset. We get a good description of our experimental data when using $\delta_{bg} = -0.24 \pm 0.05\pi$, $\delta_{ab} = 0.97 \pm 0.05$, and as an absorptive parameter for the impurity $\delta_{ab}^{\text{imp}} = 2.1 \pm 0.4$ (Fig. 3). The curve reproduces well the asymmetry with respect to energy. The values are comparable to those found by Fiete *et al.*,⁶ who found (in our notation) $\delta_{bg} = -0.25 \pm 0.1\pi$, $\delta_{ab} = 1.5 \pm 0.25$ for Co adsorbed on Cu(111).

The result shows that the electrons do not experience a phase shift of $\pi/2$ at E_F (i.e., $\delta_{bg} = 0$) as might be expected from the Anderson model of a single spin-1/2 impurity. As mentioned by Fiete *et al.*⁶ the observed background phase shift on the Co adatom might be due to charge screening. It could, however, also be a manifestation of the close d resonance. Since T_K is controlled by the position and width of this resonance the influence should be larger for Co on Ag(111) than for Co on Cu(111).

With the determination of the phase shift we have (for the case of s -wave scattering) the Green’s function of a single Co atom interacting with the Ag(111) surface state. Using the obtained $\delta(E)$ in the expression for the T matrix [Eq. (1)] we can determine the spatial dependence of the dI/dV line

shape on the lateral tip-adsorbate distance. Using Eq. (5) of Ref. 4 we obtain for the differential conductance at the site of the Co atom a Fano line with parameter $q \sim 3$, i.e., a peak rather than the observed dip. This striking difference shows that the surface-state electrons play a minor role in determining the line shape of the on-atom spectrum (Fig. 2). This is in agreement with the experimental observation that the surface-state onset is not seen generally in dI/dV spectra taken on top of adatoms.¹ However, the surface-state electrons do interact with the Kondo impurity as shown by this work and that of Ref. 3. Theory proposed⁴ that in this case one should be able to observe a spatial oscillation of the dI/dV line shape with lateral tip-adsorbate distance. The line shape should vary from diplike to peaklike shapes with the wavelength of the surface-state electrons at E_F . We find dI/dV spectroscopy not to be sensitive enough for this observation, consistent with Ref. 5. It is important to note, however, that the spatial variation would not—in the limit $r \rightarrow 0$ —yield the line shape found on the atom since it is given by the surface-state Green's function and the T matrix describing the impurity scattering.

We conclude that we have measured the phase shift that surface-state electrons experience when scattering at a single magnetic impurity which forms a Kondo state. The phase shift becomes apparent in the standing-wave pattern that the surface-state electron density forms around the magnetic adatom and is related to the fact that electrons scatter resonantly at E_F if the Kondo state is formed. The analysis of STM topographic data reveals this resonant form of the phase shift (i.e., that the phase shifts by π when crossing the resonance) and allows to extract a background phase shift for energies below E_F that is not equal to zero. With the determination of the scattering T matrix for the scattering of the surface-state electrons at the Co adatom, we can compare the experimental on-atom spectrum with what might be expected from the interaction with the 2DEG alone. We find a clear discrepancy between the two results, which indicates that the surface-state electrons play a minor role in forming the on-atom spectrum.

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