Scanning tunneling spectroscopy of transition-metal impurities at the surface of gold

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The magnetic properties of an impurity atom vary greatly depending on the nature of the impurity d level. We have used scanning tunneling spectroscopy to systematically probe the local electronic structure of individual transition-metal impurities having different d-level configurations. Atoms from the $3d$ row of the periodic table were adsorbed onto a Au(111) substrate and spectroscopically probed with an ultrahigh vacuum scanning tunneling microscope at a temperature of 6 K. Elements near the center of the $3d$ row (V, Cr, Mn, and Fe) displayed featureless electronic structure over the energy range studied, while elements near the ends of the row (Ti, Co, and Ni) showed narrow resonances near the Fermi energy. These spectroscopic features are interpreted as a combination of the Kondo resonance and bare d resonance, and are consistent with trends observed in the Kondo temperature of bulk impurities.

Magnetic impurities in a metallic host form one of the simplest correlated electron systems, but exhibit surprisingly complex phenomena. Atomic-scale magnetism and the Kondo effect both arise from an interplay between the d orbital of a transition metal impurity and surrounding conduction electrons.[1–3] This relationship results in a range of possible behavior, as any variation in the properties of the impurity d level strongly affect the formation of the many-body Kondo screening cloud.[3–5] Such behavior plays a major role in determining the form of the density of states (DOS) of a magnetic impurity.[3–5] Traditionally, photoemission has been used to study the d-level DOS of dilute magnetic alloys, but these studies have yet to resolve any signatures of the Kondo effect.[6–9] Single-impurity Kondo behavior has been observed in photoemission studies of rare-earth compounds,[10] but this interpretation is complicated by the existence of a Kondo lattice in those materials.[11] Scanning tunneling spectroscopy (STS) provides a powerful new technique for studying the local DOS around individual magnetic impurities.[12–17] STS is ideal for studying low-energy structure near the Fermi energy (E_F) since it allows access to states both above and below E_F, and has an energy resolution limited only by $k_B T$.[18] STS has already been used to study the Kondo effect for individual Co (Refs. 16, 19, and 20) and Co (Ref. 17) impurities at noble metal surfaces.[21] In order to better understand the connection between magnetism and impurity electronic structure, it is useful to apply this technique to study transition-metal impurities having different d-level configurations.

Here we report a spectroscopic survey of the low-energy electronic excitations of individual transition metal atoms adsorbed to a Au(111) substrate at 6 K. We have systematically studied different impurity elements across the $3d$ row of the periodic table in order to observe impurity trends while varying such parameters as d-orbital energy, d-orbital filling, and wave-function extent. Our measurements reveal a range of behavior for elements having partially filled d orbitals. Atoms near the middle of the $3d$ row (such as V, Cr, Mn, and Fe) show no discernible DOS features at low energy, while atoms near the ends of the row (such as Ti, Co, and Ni) show narrow resonances near E_F. These results can be qualitatively understood in terms of the Kondo effect and the Anderson model,[3] but questions remain.

The experiments were performed using a homebuilt STM contained in ultrahigh 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 using calibrated e-beam evaporator sources (typical transition metal coverages were 0.003 monolayer so that adsorbed atoms were well separated). 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. Local spectroscopic measurements were performed by placing the tip of the STM directly above isolated impurity atoms and measuring dI/dV with the STM feedback loop opened. Each $3d$ element was studied for dozens of different impurity atoms under different tip conditions, and for different sample-cleaning/deposition runs.

The results of these measurements can be seen in Fig. 1. Elements near the middle of the $3d$ row (V, Cr, Mn, Fe) are seen to yield spectra that are essentially flat in the energy range ± 100 mV around E_F. Near the ends of the $3d$ row, however, the situation is quite different. Ti atoms, located near the beginning of the $3d$ row, show a 130 mV-wide [full width at half maximum] resonance just above E_F (the full resonance is better seen in the broader energy spectrum shown in the inset to Fig. 1). Close inspection of the top curve in Fig. 1 shows that the Ti resonance has a low-energy shoulder located almost directly at E_F. This feature was consistently observed in high-resolution measurements taken on different Ti atoms with different tips. Near the opposite end of the $3d$ row, Co atoms show a narrow, asymmetric resonance near E_F that is identical to spectra reported in an earlier study.[16] The bottom curve in Fig. 1 shows a high resolution spectrum measured over a single-Ni atom. Ni atoms display a narrow resonance just below E_F, which has a distinct low energy shoulder. The broader energy spectrum seen in the inset reveals a second Ni feature (marked ''B'') that has a width of 70 mV and is located about 200 mV below E_F.
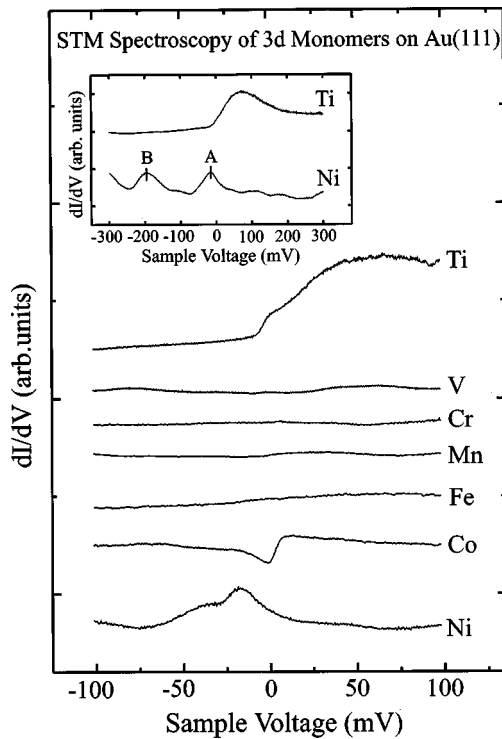
FIG. 1. dI/dV spectra taken with the STM tip held over individual transition metal impurities on the surface of Au(111) at $T = 6$ K (curves have been shifted vertically). Zero bias voltage corresponds to E_F. Inset shows spectra for Ti and Ni monomers over a broader energy range (but with lower resolution).

STM images of adsorbed transition metal atoms show that the heights of the atoms are quite comparable under typical imaging conditions (the average atomic height is 0.8 Å for $V = -0.10$ volt and $I = 0.5$ nA). This can be seen in Fig. 2, which shows an image of a 50 Å patch of the Au(111) surface after deposition of both Co and Ni atoms (compare atoms ''A'' and ''B,'' for example). dI/dV measurements allow such seemingly ''identical'' atoms to be unambiguously differentiated via their spectroscopic fingerprints. Atoms A and B of Fig. 2 are thus identified as Co and Ni, respectively, from the spectra shown in the inset. Such dI/dV spectra were observed to remain generally indepen-
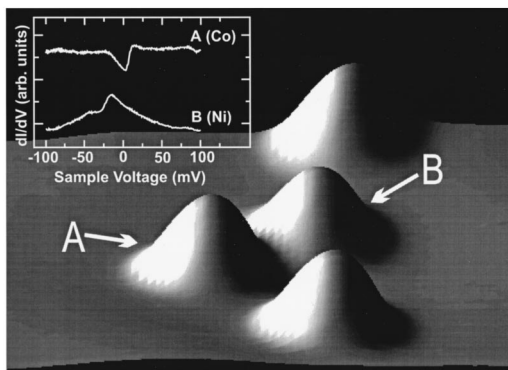

FIG. 2. Constant current STM topograph (50 Å across) of Co and Ni atoms adsorbed to Au(111) at $T = 6$ K (larger background feature is a cluster of atoms). Inset shows dI/dV spectra measured with STM tip held over atoms A and B. Spectral fingerprinting allows the identification of atom A as Co and atom B as Ni.

dent of interatomic separation until the distance between atoms was reduced below 10 Å.

In order to interpret dI/dV spectra measured for individual transition metal atoms, it is useful to understand that STS probes the local density of states of electron-like excitations for $V > 0$ and hole-like excitations for $V < 0$.[18] At temperatures above the Kondo temperature (T_K), the process of removing an electron from the impurity d orbital leads to a resonance at the ''bare'' d energy, ε_d, while the process of adding an electron leads to a bare d resonance at $\varepsilon_d + U$ (here U is the correlation energy that results from the Coulomb repulsion between two electrons in the d orbital).[1,3] The widths of such resonances have been calculated using density functional (DF) theory,[22-24] and have been measured using both photoemission[6-9] and STM spectroscopy.[12-14] Typical widths are on the order of 100 mV, although crystal field effects may split the d level by a comparable amount.[5,24] At temperatures below T_K, however, the lowest energy excited states come from a dense set of collective excitations known as the Kondo resonance.[3,25] The width of the Kondo resonance is on the order of T_K, and is exponentially sensitive to the energy location of the bare d resonance (as well as the spatial characteristics of the d orbital).[3,26] If the bare d resonance approaches E_F, then T_K rapidly increases. If the d resonance intersects E_F, then the impurity enters the ''mixed valence regime'' and is characterized by an extremely high T_K (and correspondingly broad Kondo resonance).[3,4,27] Previous measurements for ensembles of magnetic impurities imply that T_K is low for impurity elements located near the middle of the $3d$ row, and is high for elements near the ends of the row.[2,25] This behavior may be explained by shifts in the energy position of impurity d resonances for different elements across the $3d$ row.[25]

Our measurements on single-magnetic impurities at a surface follow this general trend. For the ''middle'' elements (V, Mn, Cr, Fe) we see no Kondo resonance, which can be explained by T_K being less than the experimental temperature of 6 K for these elements. Such low-Kondo temperatures are consistent with the impurity d resonance lying far from E_F. For the ''end'' elements (Ti, Co, Ni) we see features near E_F that are likely due to a combination of the Kondo resonance and bare d resonances. This is consistent with the end elements having higher T_K, and d resonances that are correspondingly closer to E_F.

At the ''low-d filling'' end of the $3d$ row, the spectroscopic structure seen for individual Ti atoms can be fit by a sum of two Fano[16,17,28] resonances. One of these resonances lies just 3 ± 2 mV below E_F and has a width of 12 ± 2 mV, while the other lies 36 ± 4 mV above E_F and has a width of 127 ± 5 mV. Figure 3 shows one particular fit to the Ti spectrum, although the data can be equally well fit over the specified uncertainty range. The higher energy resonance is reminiscent of features seen in inverse photoemission measurements of Ti alloys,[8] and most likely arises from a Ti bare d resonance (an s or p resonance would be expected to have much greater width[23]). The feature at E_F, however, appears too narrow to be a bare d resonance. The most straightforward explanation for this feature is that it is a Ti Kondo resonance. This implies that Ti atoms at the surface of gold are magnetic, but that the moment is screened with a Kondo temperature of about 70 K.[16] Such a scenario is con-
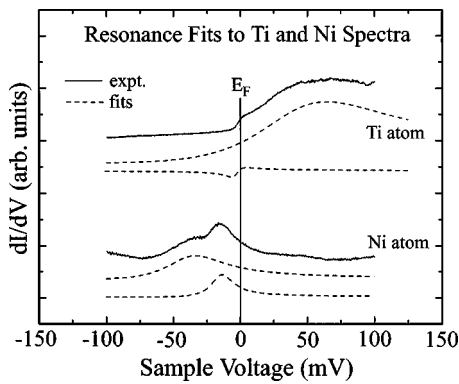
FIG. 3. High resolution dI/dV spectra for Ti and Ni monomers shown with corresponding theoretical decomposition into adjacent Fano resonances (curves have been shifted vertically). Each experimental spectrum is well fit by the sum of a narrow Fano resonance near E_F and a broader resonance located further out in energy.

sistent with DF calculations that predict moment formation for Ti surface impurities,[29] as well as the weakly magnetic (i.e., screened, $T < T_K$) behavior seen in previous Ti impurity measurements.[30]

Co and Ni both lie near the opposite end of the $3d$ row, where the d level is nearly filled. As discussed in Ref. 16, the asymmetric resonance observed for Co atoms is well fit by a Fano resonance having a width of 12 mV, and is explained as a Kondo resonance with $T_K \approx 70$ K. The Ni spectrum, on the other hand, shows more complex behavior and is best fit by the sum of two Fano resonances. One of these resonances is centered at 16 ± 1 mV below E_F with a width of 20 ± 6 mV, while the other is centered 36 ± 3 mV below E_F with a width of 37 ± 17 mV. Figure 3 shows one particular fit to the Ni spectrum, although the data can be equally well fit over the specified uncertainty range. The feature at 36 mV is most likely a bare d resonance, as it is too narrow to be an s or p resonance and is significantly offset from E_F (this feature is narrower than the Ti d resonance, consistent with the fact that elements at the end of the $3d$ row are expected to have less extended d orbitals than elements near the start of the row[31]). The resonance nearer to E_F, however, is more difficult to identify. Its width is at the borderline where one might consider it to be either a bare d resonance or the broad-

ened Kondo resonance of a mixed valence impurity (a high T_K and correspondingly broad Kondo resonance would be consistent with the proximity of the lower energy d resonance to E_F). Ni adsorbates have been predicted to display a surface magnetic moment,[32] and nonmagnetic (i.e., screened) behavior has been previously observed for Ni impurities.[30] This lends weight to the high T_K interpretation of Ni adsorbate behavior.

The Ni feature seen at even lower energy (feature ''B'' in the inset to Fig. 1) is most probably a d-resonance split off by crystal-field interactions.[5] This assignment is made on the basis of the width of the resonance and the fact that the separation between features A and B is an order of magnitude less than any expected correlation energy split.[25] It is interesting to note that this implies that the STM is able to resolve d resonances having nonzero azimuthal quantum number (m), despite the fact that one might expect such states to contribute little to the STM current based on tunnel matrix element considerations.[23,24]

In conclusion, we find that the spectroscopic properties of transition metal adsorbates vary significantly as we move across the $3d$ row of the periodic table. This behavior is best understood in the context of the Kondo effect, in which case the trend in T_K values resembles what is seen for bulk impurities and is also consistent with the observed location of d-state spectroscopic features. The most interesting new data is seen for Ti and Ni impurities, both of which appear to show Kondo behavior. These impurities show spectroscopic features that can be interpreted as a mixture of the bare d resonance and the Kondo resonance, with Ni being more strongly in the mixed valence regime. Questions do remain concerning the absolute identification of observed features, as well as the reason why particular d resonances appear in the spectra and others do not. Such questions might be addressed through further studies of the temperature and magnetic field dependence of these spectroscopic features.

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