Observation of spectral evolution during the formation of a Ni₂ Kondo molecule

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We have used atomic manipulation and scanning tunneling spectroscopy to study the evolution in electronic properties that occurs as two Ni atoms are merged into a single magnetic molecule on Au(111). We observe energetic shifting of molecular d-orbitals and a strong decrease in the molecular Kondo temperature as Ni-Ni separation is reduced to 3.4 ± 0.3 Å. These results are qualitatively explained by a combination of a spin-$\frac{1}{2}$ s-d model and density-functional calculations.

Condensed-matter behavior is fundamentally determined by the evolution in electronic properties that occurs as atoms are brought together into a solid. In magnetic nanostructures this often leads to an interplay between extended s-like states and more localized d orbitals. As atoms merge, subtle changes in orbital overlap and symmetry cause charge to shift from one atomic state to another, leading to a variation in local magnetic moments and exchange interactions.[1,2] Although such microscopic properties are usually inferred from macroscopic observations, recent advances in scanning tunneling microscopy (STM) have opened the possibility of probing local interactions in magnetic structures assembled atom by atom at surfaces.[3–5]

At a surface, however, atomic scale magnetic structures can interact with the electronic degrees of freedom of the substrate, leading to the Kondo effect.[4,6–9] The Kondo effect causes a singlet to form as the collective ground state of a local magnetic moment and conduction electrons at low temperature.[10] When magnetic atoms are combined on a surface Kondo singlet formation competes with interatomic magnetic interactions to determine the magnetic ground state. This competition has been studied theoretically for a single pair of interacting Kondo impurities,[11–15] and a range of behavior has been predicted that includes two-stage screening transitions[12,13] and a non-Fermi-liquid regime.[15] These studies have relevance for correlated materials behavior, but there have been few attempts to directly observe the effects of pairwise interactions between a single pair of Kondo impurities.[3] As device sizes approach the nanometer length scale, however, understanding such interactions for discrete systems becomes ever more important.

Here we report a STM study of the evolution in electronic properties of two Ni atoms as they are pushed together on a Au(111) surface via atomic manipulation. Using local spectroscopy we have directly observed a level shifting of Ni₂ molecular d orbitals for different Ni-Ni separations down to 3.4 ± 0.3 Å. In addition to "bare" electronic states, however, we have also measured the evolution of the many-body Kondo resonance as two Ni atoms form an interacting "Kondo molecule." This work is unique because of the continuous evolution observed in molecular electronic states as a function of interatom separation. In order to gain insight into the electronic changes observed in Ni-Ni Kondo molecules, we have calculated the theoretical electronic structure of Ni₂

for different interatomic separations using density-functional theory. We find that dimerization causes the Ni $4s$ orbitals to strongly hybridize with each other, leading to a local charge redistribution that explains the experimentally observed d-level shifting. Ni₂ Kondo behavior can be qualitatively understood through the behavior of the highest occupied molecular orbital and the amount of d-level hybridization between Ni atoms.

The experiments were performed using a homebuilt STM contained in ultrahigh vacuum (UHV) and cooled to 7 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 7 K and dosed in UHV using a Ni e-beam evaporation source. dI/dV spectra were measured using a lock-in detection of the ac tunnel current driven by a 450-Hz, 1-mV (rms) signal added to the junction bias under open feedback conditions. Atomic manipulation of Ni atoms was carried out using the "sliding" procedure with the tip of the scanning tunneling microscopy.[16]

Figure 1(A) shows the process of fabricating a Ni dimer at the surface of gold in three successive steps. From our studies of ~20 dimers we have identified four important stages in the formation of Ni₂ on Au(111). These are seen in Fig. 1(B), where all images shown were acquired with the same STM tip for meaningful comparison. The first stage, monomers, are defined as single Ni atoms at least 12 Å from any neighbors (center-to-center). The second stage occurs when Ni atoms begin to noticeably overlap at a separation of about 7 Å. Here the two atoms are still distinct, but hybridization effects are visible. The third and fourth stages occur when two Ni atoms have fully merged into a dimer structure and individual atoms are no longer distinct. An estimate of the distance between atoms is obtained by fitting the monomer with a Gaussian profile and then fitting the different dimer stages with a sum of two such Gaussians. This procedure yields an interatom separation of 6.9 ± 0.2 Å for stage No. 2 dimers, a separation of 4.0 ± 0.3 Å for stage No. 3 dimers, and a separation of 3.4 ± 0.3 Å for stage No. 4 dimers. These distances match closely to expected distances between threefold hollows on the Au(111) surface, as seen in the inset to Fig. 1(B).

In order to study the evolution of Ni₂ electronic structure as a function of interatomic separation, STM spectroscopy was performed on Ni atoms during all four stages of dimer
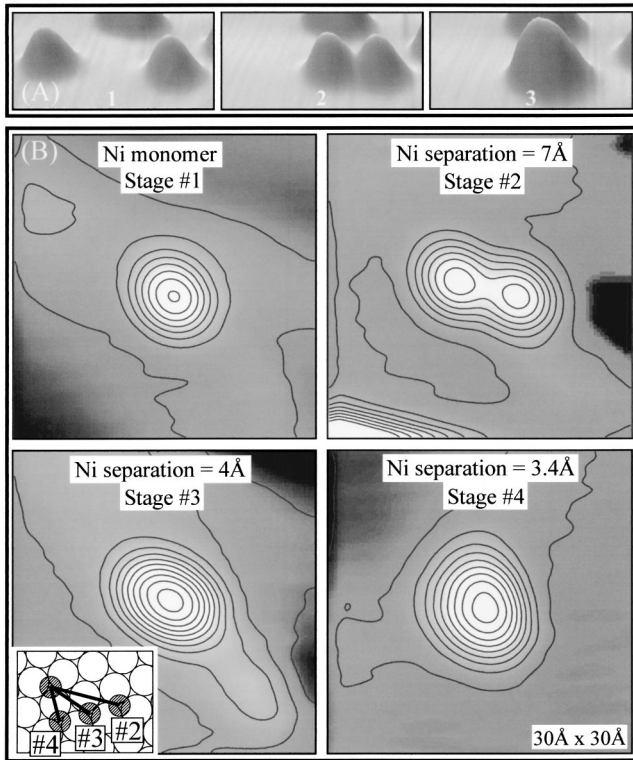
FIG. 1. (A) Process of fabricating a Ni dimer from two Ni monomers on Au(111) using atomic manipulation. (B) 30×30 Å^2 topographs showing the four most important stages of Ni dimer formation on Au(111) ($I = 0.5 \times 10^{-9}, V = 100$ mV, $T = 7$ K).
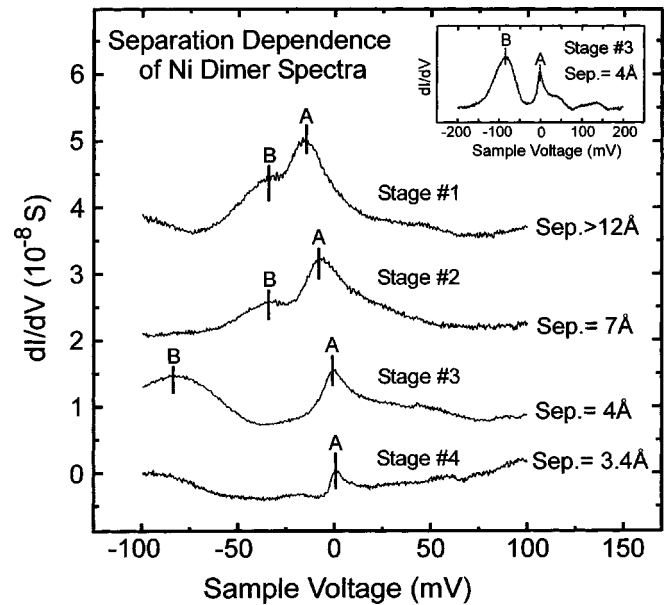

FIG. 2. dI/dV spectra taken with a STM tip held over Ni atoms for different Ni-Ni interatomic separations on Au(111). Spectra for stages Nos. 2, 3, and 4 have been shifted vertically by -1.5, -3, and -4.1×10^{-8} S, respectively ($T = 7$ K).

formation. As seen in Fig. 2, Ni monomers display a double-peaked resonance with most spectral weight located below E_F. These two peaks (labeled A and B) exhibit an evolution in behavior as two Ni atoms are merged into a Kondo molecule. Peak A shifts upward toward E_F and remains essentially constant in width as the Ni-Ni separation is reduced down to 4 Å. At the closest separation of 3.4 Å, however, the width of peak A dramatically narrows. At this separation peak A is observed to be spatially localized near the outer regions of the dimer at a radius of 5 ± 1 Å, and to have a zero amplitude near the dimer center. Peak B, on the other hand, shifts downward in energy as the Ni atoms are brought to within 4 Å of each other. This is perhaps best seen in the inset to Fig. 2, which shows the spectrum out to ± 200 mV for a Ni-Ni separation of 4 Å. At the closest approach of 3.4 Å, however, peak B disappears and cannot be observed within a range of ± 300 mV from E_F. The observed spectra were each fitted by a sum of two Fano resonances[17] in order to quantitatively determine the dependence of peak widths and energies on Ni-Ni separation. These values are plotted in Fig. 3.

A central question for understanding the behavior of the Ni$_2$ Kondo molecule is the physical origin of resonances A and B, and the mechanism by which they evolve as the Ni-Ni distance is decreased. One possible origin for the observed resonances is the $4s$ atomic orbital of Ni. This will hybridize with substrate conduction levels to create a resonance near the bare s-state energy.[18] s resonances are expected to have

widths >500 meV,[18] however, much too wide to explain resonances A and B. Another possibility is that the resonances arise from the $3d$ states of Ni. Such states are expected to have widths in the 100-meV range,[19,20] and so provide a good explanation for resonance B which has an experimentally observed width of ~50 meV. Resonance A, on the other hand, has a width of only 7 meV at the closest Ni-Ni separation. This is much too narrow to be explained as a "bare" d resonance, and so we identify it with a third possibility: the Kondo resonance.
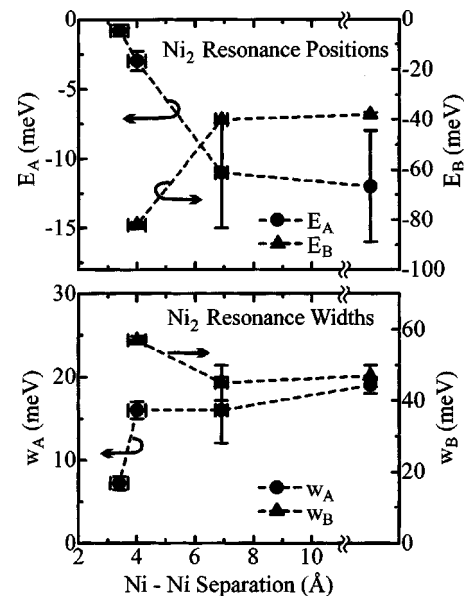

FIG. 3. Evolution in energy and width of experimentally observed resonances A and B as a function of Ni-Ni separation. Values were determined by fitting two Fano line shapes to each spectrum.

The Kondo resonance arises due to the formation of a highly correlated spin-screening cloud from conduction-band electrons surrounding a magnetic impurity.[10] This screening cloud leads to a resonance in the density of states that is located at E_F and has a width $2k_B T_K$ for $T \ll T_K$ (T_K is the Kondo temperature).[10] The half-width of resonance A thus reveals that T_K for Ni_2 remains nearly constant at 100 ± 20 K for Ni-Ni separations $\geqslant 4$ Å, but drops sharply to 42 ± 5 K at the closest separation of 3.4 Å. For a single spin-$\frac{1}{2}$ s-d model, such a Kondo behavior is regulated by the d-orbital magnetic moment through the exchange constant J, which couples the d orbital to conduction electrons:[10]

$$\rho J \approx \frac{1}{2\pi} \frac{\Gamma U}{(E_d - E_F)(E_d + U - E_F)},$$

$$k_B T_K = D |2\rho J|^{1/2} e^{-1/2\rho J}. \tag{1}$$

Here D is the bandwidth of the substrate, ρ is the local density of states, Γ is the width of the d-orbital resonance, E_d is its energy location, and U is the Coulomb repulsion between two electrons in a d orbital. In a Kondo molecule, however, Kondo behavior will be modified by interatomic interactions and the existence of a multiplicity of molecular d orbitals.

In order to gain greater insight into the effect these molecular interactions might have on the Ni_2 Kondo system, we used the local spin density approximation[21] (LSDA) to calculate the electronic structure of a Ni_2 molecule at different interatomic separations. These calculations do not include many-body correlations due to the Kondo effect, but we believe they provide a useful starting point for gaining a qualitative understanding of the s- and d-state hybridization and level splitting that occur during Ni_2 molecule formation.[19] For example, this allows us to check some parameters used in simplified models, such as the location of d orbitals, the strength of the impurity potential, and the magnetization of the molecule. The calculations employed a Ni pseudopotential in a plane-wave basis and were done in a supercell. In Fig. 4(A) we plot the calculated total charge density around a free Ni_2 molecule for three interatomic separations meant to model the experimental dimer formation. At the largest separation of 8.5 Å, we observe essentially no hybridization between either the $4s$ or $3d$ orbitals, and the atomic Ni ground state $3d^9 4s^1$ is obtained. At a separation of 6 Å, however, the $4s$ orbitals overlap and charge redistribution occurs, leading to molecular orbital formation for the $4s$ orbitals and to $4s$ and $3d$ energy-level splittings. These effects become even more significant as the interatomic separation is decreased. The d-orbital density, however, remains atomiclike for separations down to 4 Å, and there is only negligible interatomic d-d hybridization for separations $\geqslant 4$ Å.

The most important d levels for Kondo behavior are those near E_F, as these are most strongly exchange coupled to conduction states [Eq. (1)]. For Ni-Ni separations $\geqslant 4$ Å we identify two Ni_2 molecular orbitals from our calculations that lie closest to E_F. These states derive from odd (σ_u) and even (σ_g) combinations of the minority spin $3d_{3z^2-r^2}$ orbitals from the two Ni atoms ($\mathbf{z}$ is parallel to the line joining them), and their energy trajectories are shown in Fig. 4(B).
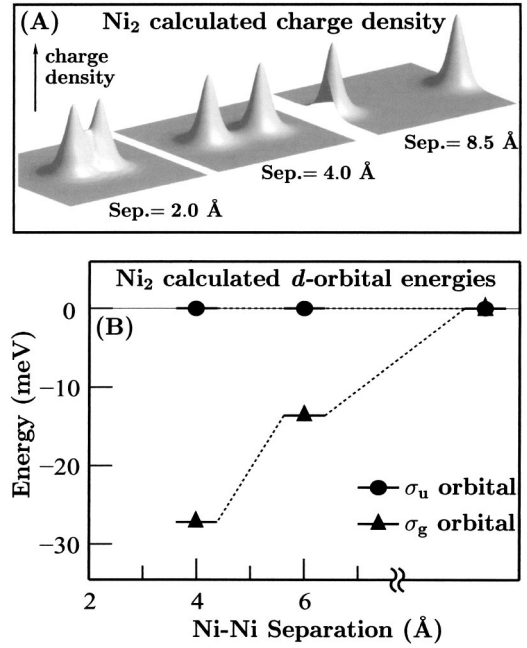

FIG. 4. (A) Calculated total electronic density for a free Ni_2 molecule having different Ni-Ni separations (the density shown occurs 1 Å above dimer plane). (B) Calculated energetic locations of two molecular d orbitals closest to E_F for different Ni-Ni separations.

For an isolated Ni dimer, σ_u is unoccupied. To understand the influence of the surface we constructed a large supercell containing a Ni dimer and 100 Au atoms in four layers. We then used the lowest combination of atomic orbitals method to compute the ground-state properties of the stage No. 3 dimer configuration. The presence of a Au surface causes a reduction of magnetization and a charge transfer of ~0.25 electrons into the Ni dimer. As a result of the charge transfer, the σ_u state should be pinned at E_F within a one-electron theory. The Ni_2 σ_g state is seen to disperse downward relative to the energy position of σ_u as the atoms are brought together. This decrease in energy is comparable in order of magnitude to what is observed experimentally for resonance B, and so we identify resonance B as originating from a σ_g molecular orbital. The σ_u level, on the other hand, is expected to remain close to E_F for Ni-Ni separations $\geqslant 4$ Å, and so we believe this state has the strongest influence on T_K.

For Ni-Ni separations less than 4 Å, our calculations show a dramatic change in the electronic structure of Ni_2. The d levels begin to overlap strongly in this regime, and there is significant interatomic mixing, energy-level splitting, and reordering. The σ_u and σ_g states, for example, shift down far from E_F. At a Ni-Ni separation of 2 Å we find that the highest occupied molecular orbital is an even superposition of $4s$ orbitals (a bonding state), and the closest d level (π state) lies 70 meV below this. These shifts in the d-level position provide a possible explanation for the sudden drop in T_K that is experimentally observed for Ni-Ni separations of 3.4 Å. In analogy to the single impurity model of Eq. (1),

we expect T_K to drop as d levels move away from E_F. Alternatively, the observed drop in T_K might also be explained by a sharp increase in magnetic exchange coupling between Ni atoms as their d orbitals begin to strongly overlap at close distances. Such a coupling has been predicted to reduce T_K in multiple impurity systems,[11,12] and is consistent with predictions of interatomic ferromagnetic exchange energies as high as 390 meV in free Ni_2 molecules.[22] Although we expect weaker magnetic coupling in the more extended Kondo molecule, a ferromagnetic interaction of order T_K (only ~9 meV) should be sufficient to perturb the Kondo behavior.[11–13]

In conclusion, we have measured the evolution of molecular orbitals and Kondo behavior as two Ni atoms are merged into a Kondo molecule at the surface of gold. In the regime where Ni-Ni separation $\geqslant 4$ Å these results are qualitatively explained by LSDA calculations that show Ni_2 d-level splitting in response to the interaction between the $4s$ orbitals of the two Ni atoms. At the closest Ni-Ni approach of 3.4 Å we observe a sharp drop in molecular T_K that can be explained by the onset of strong d-d hybridization.

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