# Kondo Response of a Single Antiferromagnetic Chromium Trimer

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The triangular Cr trimer ($Cr_3$) is a fundamental component in a number of frustrated, antiferromagnetic systems. We have used atomic manipulation and scanning tunneling spectroscopy to probe the local behavior of this basic magnetic substructure by fabricating and analyzing individual Cr trimers at the surface of gold. We find that Cr trimers can be reversibly switched between two distinct electronic states. This phenomenon can be explained as the Kondo response of a spin-switching, magnetically frustrated nanocluster. Such behavior is consistent with noncollinear magnetic states predicted for Cr trimers whose structures differ by the position of a single atom.

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The competition between exchange and bonding interactions in transition metal nanostructures leads to rich magnetic behavior [1]. Subtle rearrangements of atoms can dramatically change magnetic ground states, as seen in a variety of nanocluster systems [2,3]. Systems exhibiting magnetic frustration display even greater complexity, as constituent atomic spins cant away from symmetry axes [4–7]. These “noncollinear” effects are expected to play an important role in the magnetic properties of nanostructures due to bonding anisotropy and reduced symmetry [4,5].

Cr nanoclusters form an ideal system to examine such effects. Cr is unique because its half-filled valence configuration ($3d^5 4s^1$) yields both a large atomic magnetic moment and strong interatomic bonding, leading to magnetic frustration and complex spin phenomena [8,9]. The simplest and most fundamental Cr system to exhibit such behavior is the trimer ($Cr_3$), which has been predicted to display a variety of noncollinear magnetic structures [6,7].

Examining individual trimers is difficult, but the scanning tunneling microscope (STM) provides an excellent tool for atomically fabricating and characterizing these magnetic nanoclusters and for determining their behavior in a solid-state (i.e., “devicelike”) setting. This can be seen from recent STM studies of the interplay between magnetic and electronic phenomena in atomically fabricated magnetic dimers [10], quantum corral cavities [11], and spin-polarized nanostructures [12]. When atomic-scale magnetic structures are connected to conducting substrates, however, coupling between magnetic and electronic degrees of freedom can lead to correlated magnetic screening via the Kondo effect [13]. This influences the electronic density near a magnetic nanostructure and modifies its magnetic response. Such behavior has been studied in the context of one [11,14,15] and two [10] impurity systems, but it has yet to be examined in more complex magnetic structures, such as trimers.

Here we report an STM study of the local electronic properties of artificially fabricated Cr clusters having up to three Cr atoms on a gold surface. Cr atoms were deposited onto clean Au(111) at 7 K and manipulated with the tip of an STM to form artificial dimers and trimers. The low-energy excitation spectra of these structures were investigated using STM spectroscopy. While single Cr atoms and Cr dimers show no structure in their excitation spectra, two distinct behaviors are observed for compact, triangular Cr trimers. One class of compact Cr trimer exhibits a featureless low-energy spectrum while the other displays a narrow resonance at $E_F$ having a width of only 5 mV. This resonance can be explained as the Kondo response of a frustrated, antiferromagnetic nanocluster. Differences in electronic behavior between these two classes of trimers are explained by predicted structural switching between noncollinear magnetic states having zero and nonzero moment [7].

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 calibrated *e*-beam evaporation source. $dI/dV$ spectra were measured using 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.

Cr dimers and trimers were fabricated using atomic manipulation with the STM tip. Figure 1 shows the process of arranging three Cr atoms into a compact trimer at 7 K (sliding resistance $= 2 \times 10^5\ \Omega$ [16]). A variety of different structures is possible for trimers. The left panel of Fig. 2 (trimer *A*), for example, shows a linear trimer constructed so that Cr atoms occupy next-nearest neighbor sites on the Au(111) lattice (Cr-Cr distance = 5.8 Å). It was not possible to build linear trimers using nearest-neighbor sites because Cr atoms spontaneously rearranged into compact triangular shapes when brought so close. Such compact trimers can be seen in the second and third panels of Fig. 2 (trimers *B* and *C*). Trimer *C* of Fig. 2 shows the same three atoms as trimer *B*, but they have been slightly rearranged by sliding trimer *B* 4 Å across the surface as a

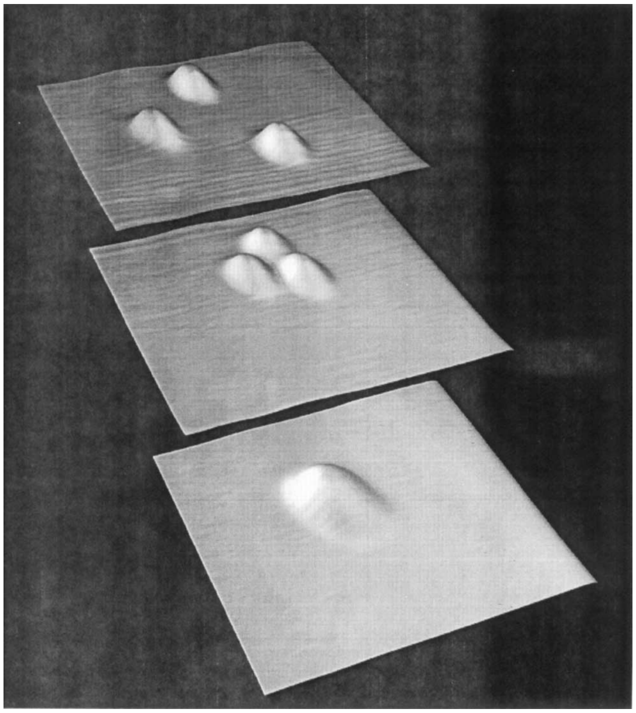

FIG. 1. Constant current topograph (70 Å × 70 Å, $I = 5 \times 10^{-9}$ A, $V = 0.10$ V) showing the fabrication of a compact triangular trimer from three Cr atoms on Au(111) ($T = 7$ K).

unit with the STM tip (sliding resistance $= 2 \times 10^5\ \Omega$). Individual atoms cannot be resolved in the compact shapes when interatom distances are less than 5 Å. The internal structure of trimers *B* and *C*, for example, are clearly different as seen by overall cluster shape, but the actual atomic positions cannot be easily distinguished.

In an attempt to clarify the observed trimer structures, we fitted an isolated Cr monomer topograph with a Gaussian surface: $z \propto e^{-a(x^2+y^2)}$, and we calculated superpositions of such surfaces positioned at likely atomic positions. This gives a rough estimate of expected trimer electron cloud distributions. The results of the density calculations are shown in the right-hand panels of Fig. 3 for a linear trimer, a compact symmetric trimer, and a compact isoceles trimer (adatom positions were constrained to the threefold hollow sites shown). The calculated density plots for these three structures came closest to the experimental trimer topographs of Fig. 2. This simple density algorithm reproduces the linear trimer topograph quite well. The compact trimers of Figs. 2(b) and 2(c) are also qualitatively reproduced by the model symmetric and isoceles structures [Figs. 3(b) and 3(c)], but our experimental resolution is not high enough to differentiate between these two structures in STM topographs.

The local electronic properties of the fabricated Cr nanoclusters were probed using STM $dI/dV$ spectroscopy. Figure 4 shows the results of measurements on several different arrangements of atoms. Cr monomers and dimers both show no spectroscopic features in the energy range ±100 mV about $E_F$. Various "loose" trimers (i.e., trimers having one interatomic separation greater than 6 Å) were also measured (not shown) and displayed no spectroscopic features in this energy range [17]. Compact triangular Cr trimers, however, exhibited two distinct classes of behavior, here referred to as "state #1" and "state #2." As seen in Fig. 4, trimers in state #1 yield a featureless spectrum, while trimers in state #2 display a narrow resonance at $E_F$. The width of the state #2 resonance is only 5 mV (FWHM), as seen in the higher resolution spectrum displayed in the inset in Fig. 4. This two-state behavior was observed for dozens of compact trimers using differently prepared tips, and the results were not sensitive to the position of the trimers on the surface. Individual Cr trimers were reversibly switched between state #1 and state #2 by perturbing their structure with the STM tip. Trimers *B* and *C* of Fig. 2, in fact, show the same compact trimer after being switched from state #1 behavior (trimer *B*) to state #2 behavior (trimer *C*) via tip manipulation (the reverse process was also accomplished for this particular trimer).

The central result of this Letter is that the feature seen at $E_F$ for state #2 Cr trimers reflects the low-energy Kondo response (i.e., the "Kondo resonance" [13–15,18]) of a single, antiferromagnetic trimer. Small variations in the trimer structure (for example, the repositioning of a single atom) change its magnetic state, thus "switching off" the Kondo effect and resulting in the observed state #1 behavior. This interpretation is consistent with recent theoretical

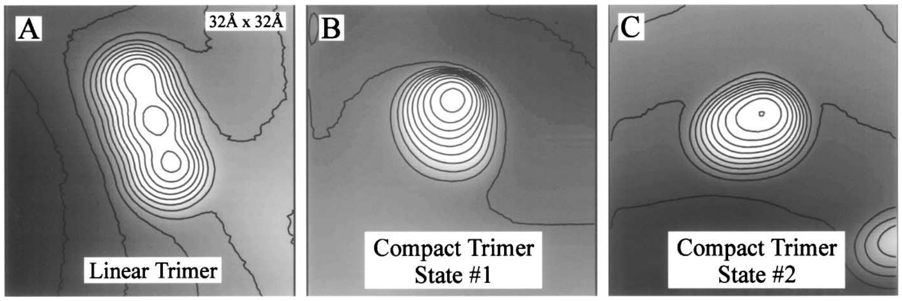

FIG. 2. Constant current topographs of three atomically fabricated Cr trimers: (A) linear trimer, (B) compact triangular trimer showing state #1 behavior, and (C) compact triangular trimer showing state #2 behavior.

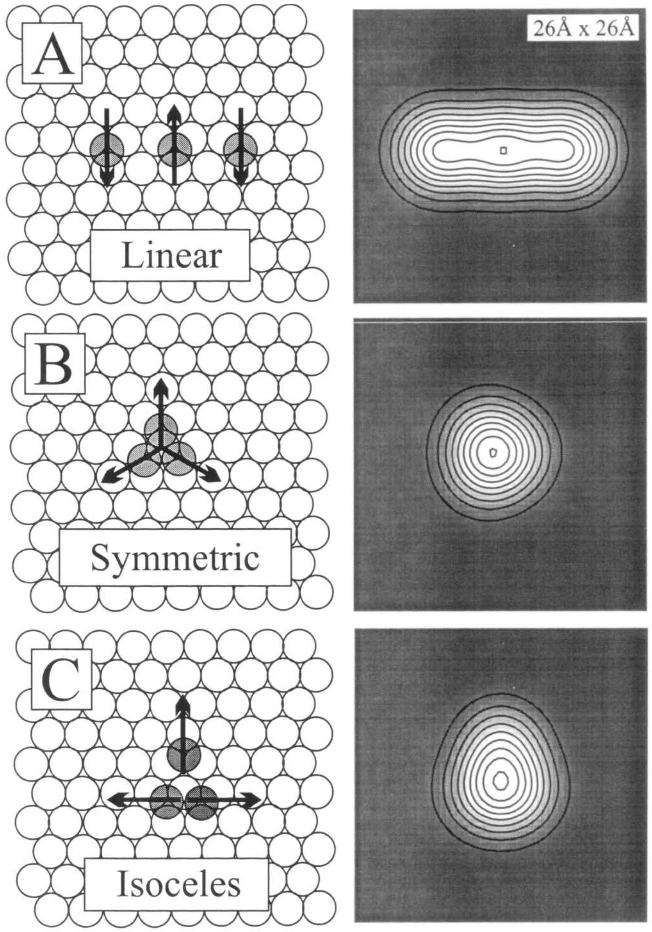

FIG. 3. Theoretical density plots on the right for three model trimer structures at left: (A) linear trimer, (B) compact symmetric trimer, and (C) compact isoceles trimer. Arrows show spin configurations predicted for these structures by Uzdin *et al.* [7].

predictions regarding the behavior of frustrated magnetic trimers [7].

We first discuss how our observations for Cr monomers and dimers fit into this physical framework. Since a Cr atom on gold is a magnetic impurity, it should form a Kondo screening cloud at temperatures below a characteristic Kondo temperature, $T_K$ [13,18]. The fact that the monomer spectrum in Fig. 4 lacks a Kondo peak implies that $T_K$ for Cr adsorbates is significantly less than the experimental temperature. This is consistent with previous studies of Cr impurities in the bulk [18] and implies a small exchange coupling constant between Cr monomers and conduction electrons [18,19]. When two Cr monomers are joined to form a dimer, strong antiferromagnetic (AF) coupling is expected between the atoms due to the intense bonding between half-filled *d* shells [8]. Such strong AF coupling should induce a net magnetic singlet between the two atoms, quenching the Kondo effect for dimers [20]. We thus expect no Kondo resonance from Cr dimers, consistent with the featureless dimer spectrum of Fig. 4.

Compact Cr trimers, on the other hand, form a frustrated AF-coupled system and so can exhibit more complex magnetic behavior than dimers [4,6,7,9]. Recently, the ground state magnetic configuration of a Cr trimer in contact with a metal host has been calculated by Uzdin *et al.* using a modified Anderson model in the Hartree-Fock approximation [7]. Uzdin *et al.* studied a range of geometries closely approximating our experimentally achieved structures. They predict that linear trimers should exhibit a collinear AF configuration and that compact trimers should produce a range of noncollinear spin structures (see sketches in the left-hand panels in Fig. 3). Equal magnetic coupling between Cr atoms in a symmetric trimer, for example, is predicted to induce 120° spin canting, yielding a net trimer magnetic moment of zero. If one Cr atom is slightly decoupled from its two neighbors, however, the resulting "isoceles" trimer is predicted to acquire a net moment. The left panel of Fig. 3(c) represents this behavior: as the topmost atom separates, the tightly coupled base pair snaps into an antiparallel AF configuration and the spin of the displaced atom aligns itself 90° from this dimer axis [7]. Neglecting spin-orbit interactions, the decoupled spin of the isoceles trimer can rotate freely about this axis.

The narrow $E_F$ resonance seen experimentally for state #2 compact trimers can be explained in this context as the Kondo response of an isoceles Cr trimer. Kondo behavior here arises from spin-flip scattering between conduction electrons and the net magnetic moment of the frustrated trimer. Alternative explanations for the resonance, such

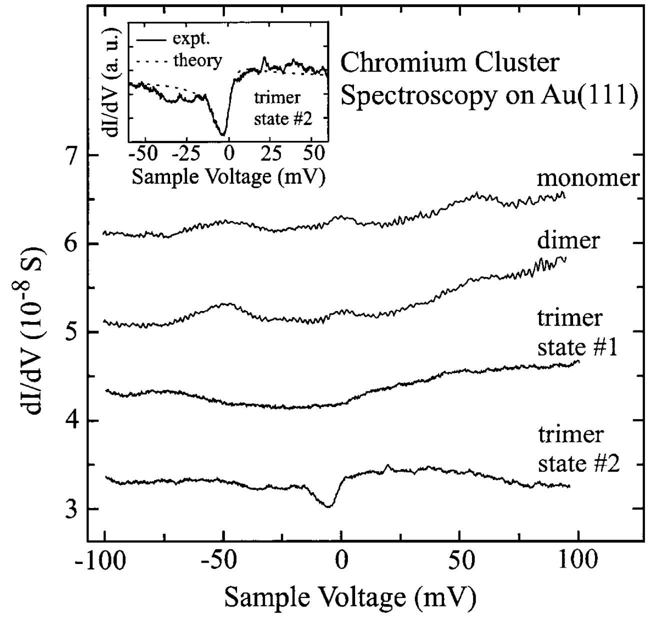

FIG. 4. STM $dI/dV$ spectra measured with tip held over the centers of a Cr monomer, a Cr dimer, a compact Cr trimer exhibiting state #1 behavior, and a compact Cr trimer exhibiting state #2 behavior. The Cr trimer in state #2 exhibits a narrow Kondo resonance at $E_F$ ($V = 0$). Curves for the trimer in state #1, the dimer, and the monomer have been vertically shifted by $1 \times 10^{-8}$ S, $2 \times 10^{-8}$ S, and $3 \times 10^{-8}$ S, respectively. The inset shows spectrum for state #2 trimer with expanded vertical scale and Fano line shape fit.

as bare atomic states, lead to features much broader than what is observed experimentally for state #2 trimers [21]. The non-Kondo behavior observed for state #1 trimers is explained by structural switching (induced by atomic manipulation) to the symmetric, zero-moment state. Assuming the symmetric state to be a singlet, the Kondo effect will be quenched in this case (since electrons cannot spin-flip scatter off of a singlet). Our observation that individual compact trimers can reversibly switch between state #1 and state #2 via small structural changes is consistent with the prediction by Uzdin *et al.* that displacement of only a single atom can cause the cluster to switch between zero-moment and non-zero-moment configurations [7].

The coupling between state #2 "Kondo trimers" and their environment can be quantified by fitting the Kondo resonance spectrum to a Fano line shape [14,22]:

$$\frac{dI}{dV}(V) = \sigma_0(V)\,\frac{(q + \varepsilon')^2}{1 + \varepsilon'^2}, \qquad \varepsilon' = \frac{e(V - \alpha)}{k_B T_K}. \tag{1}$$

Here $\sigma_0$ is the differential conductance in the absence of the trimer, $q$ is a tip-coupling parameter that determines line shape symmetry, and $\alpha$ is a constant arising from $d$-state degeneracy. As seen from the fit shown in the inset in Fig. 4, the "antiresonance" line shape arises from a low $q$ value of $0.42 \pm 0.03$. This implies weak coupling between the STM tip and trimer $d$ orbitals compared to tip coupling to continuum states [14,22] (a more complete discussion of the physical origin of this line shape can be found in Ref. [23]). Analysis of the width of the Fano line shape for four different trimers results in a trimer Kondo temperature of $T_K = 50 \pm 10$ K. Cr trimers thus experience greater exchange coupling with conduction electrons than Cr monomers, which have a $T_K$ considerably lower than the experimental temperature of 7 K. One explanation for this difference is the variation in electronic structure that exists between Cr monomers and trimers. Because Cr is positioned in the middle of the third row of the periodic table, the majority and minority $d$ resonances of a Cr monomer tend to lie away from $E_F$ [24]. This reduces exchange coupling between the Cr local moment and conduction electrons and drives down $T_K$ [18,19]. When Cr monomers are combined into a trimer, however, overlap between adjacent $d$ orbitals causes splitting among the $d$ states. This should push some states closer to $E_F$, thus increasing the exchange coupling and resulting in the higher $T_K$ seen experimentally for trimers.

In conclusion, we have observed behavior that is consistent with the Kondo effect in individual, artificially fabricated Cr trimers at a surface. Experimentally observed switching in Cr trimers can be explained by predicted variations in trimer magnetic behavior via small changes in trimer atomic structure. Further studies utilizing spin-polarized tunneling techniques [9] may be useful for clarifying the relation between atomic geometry and local spin structure in these magnetically frustrated nanoclusters.

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