Kondo State for a Compact Cr Trimer on a Metallic Surface

Yu. B. Kudasov[1,*] and V. M. Uzdin[2]

[1]*VNIIEF, Prospect Mira 37, Sarov, Nizhni Novgorod Region, 607180, Russia*
[2]*St. Petersburg State University, ICAPE, 14 linia Vasilevskij Ostrov 29, 199178, St. Petersburg, Russia*
(Received 12 February 2002; published 18 December 2002)

The ground state of a Cr trimer supported on the Au(111) surface is investigated by means of a variational approach to the Coqblin-Schrieffer Hamiltonian. The temperature of Kondo-resonance formation (T_K) for equilateral trimers increases drastically as compared to T_K for a single Cr adatom. The Kondo state of a Cr trimer proves to be very sensitive to geometry and a small shift of any atom from the symmetrical position leads to a rapid decrease in T_K. These results are in good agreement with recent observations of the Kondo response of a single antiferromagnetic chromium trimer [T. Jamneala *et al.*, Phys. Rev. Lett. **87**, 256804 (2001)].

    PACS numbers: 73.22.–f, 75.25.+z, 75.75.+a

The development of scanning tunneling spectroscopy and the ability to build clusters with well-controlled interatomic distances on metal surfaces has revived interest in phenomena associated with the Kondo effect in dilute alloys [1–3]. Probing the Kondo resonance on individual atoms [4] or very small clusters [5,6] with scanning tunneling microscopy (STM) allows the study of magnetism at a scale that cannot be achieved by other methods. Although the physics of Kondo systems was investigated and understood in detail, decades ago, new Kondo phenomena observed in the clusters on the metal substrate contain puzzles which have no explanation thus far. For one isolated magnetic impurity, the experimentally observed width and shift of the Kondo resonance are in accordance with calculations obtained from a combination of band structure and strongly correlated techniques [7], but for magnetic dimers and trimers the situation has proven to be more complicated [5,6].

Astonishing results were obtained very recently for Cr trimers on a gold surface [6]. The STM spectrum for a single Cr atom was observed not to contain a Kondo peak, implying that the Kondo temperature for Cr monomers is significantly less than the experimental temperature (7 K). When two Cr atoms are joined to form a dimer, interaction between their magnetic moments is expected only to suppress the Kondo effect, and indeed no Kondo signature was experimentally observed for these Cr dimers. Similarly, artificially fabricated cobalt dimers on Au(111) show an abrupt disappearance of the Kondo resonance for Co-Co separation less than 6 Å [5]. For trimers, one might expect that additional interactions between moments would only hinder the screening of the moments and transition to the Kondo state. In the dilute bulk CoAu alloys, for example, isolated Co atoms and dimers showed Kondo behavior (with the Kondo temperature for dimers 9 times smaller than that of isolated Co atoms), whereas groups of three or more atoms stayed magnetic at very low temperature [8]. However, Cr trimers on Au(111) do not follow such a rule [6]. Since distances between adatoms in the experimentally fabricated trimers were very small (less than 5 Å), the individual positions of the adatoms could not be clearly distinguished by STM. Nevertheless, compact triangular Cr trimers exhibited two distinct classes of behavior. In the first state, they displayed a featureless STM spectrum, whereas in the second state they displayed a narrow resonance at the Fermi level corresponding to a Kondo temperature $T_K \approx$ 50 K. This value greatly exceeds T_K for single Cr impurities on the surface, which is definitively below 6 K. Trimers were reversibly transferred from one state to the other by very small shifts of one atom via tip manipulation. It is natural to assume that the two observed states correspond to equilateral and isosceles trimer configurations. In the equilateral configuration, Cr atoms should occupy nearest neighbor sites on the Au(111) lattice (Cr-Cr distance is 2.9 Å). In the most likely isosceles configuration, two Cr atoms stay in the nearest neighbor positions while one atom is shifted to a distance of 4.4 Å (see the inset of Fig. 2) from either of its neighbors.

The ground state of a Cr trimer is noncollinear due to magnetic frustrations [9,10]. Small variations in hopping parameters have been predicted to lead to strong changes in magnetic moment orientation for constituent atoms and therefore of the total magnetic moment of a trimer. This is expected to influence low-temperature behavior but hardly can explain the (at least) order of magnitude increase of T_K for Cr trimers as compared to single adatoms.

In this Letter, we present a variational theory developed for the description of small supported clusters. This theory allows us to take into account superpositions of states in which some atoms of the cluster form Kondo singlets, whereas others conserve their magnetic moments. The transition of some atoms into the singlet state removes magnetic frustration in the clusters and compensates for the loss of Heisenberg-like magnetic energy. We will demonstrate that (i) for symmetric Cr trimers the Kondo temperature can be hundreds of times higher than

for Cr monomers and (ii) the transition from a symmetric (equilateral) to an isosceles trimer configuration leads to a rapid decrease of T_K.

To take into account the interaction of localized d states of Cr adatoms with bulk conduction electrons of the substrates, we use the Coqblin-Schrieffer Hamiltonian for few impurities [11]:

$$H_{CS} = \sum_{\mathbf{k},\sigma} \varepsilon_k c^\dagger_{\mathbf{k}\sigma} c_{\mathbf{k}\sigma} + \frac{1}{L} \sum_{j,\mathbf{k},\mathbf{k}',\sigma,\sigma'} \Gamma_{\mathbf{k}\mathbf{k}'} e^{i(\mathbf{k}-\mathbf{k}')\mathbf{R}_j}$$
$$\times \left(c^\dagger_{\mathbf{k}'\sigma'} c_{\mathbf{k}\sigma} \left[d^\dagger_{j\sigma} d_{j\sigma'} - \frac{\delta_{\sigma\sigma'}}{2} \right] \right). \tag{1}$$

Here, $d^\dagger_{j\sigma}(d_{j\sigma})$ and $c^\dagger_{\mathbf{k}\sigma}(c_{\mathbf{k}\sigma})$ are the creation (annihilation) operators for the localized $3d$ state on the jth adatom with spin σ and for the conduction electron with wave number $\mathbf{k}$ and energy ε_k, R_j is the radius vector of the jth adatom, and L is the number of lattice sites. The Cr adatoms are described as a doubly degenerate $3d$ level. We discuss the validity of this assumption below. The function $\Gamma_{\mathbf{k}\mathbf{k}'}$ can be expressed as $\Gamma_{\mathbf{k}\mathbf{k}'} = \Gamma Y^*_{20}(\Omega_{\mathbf{k}}) Y_{20}(\Omega_{\mathbf{k}'})$, where Y_{lm} are the spherical harmonics (for the sake of simplicity, we assume the projection of the Cr orbital moment on the normal to the surface to be zero).

To include interaction between the magnetic moments $\mathbf{S}_j$ in the trimer, we supplement a Hamiltonian (1) with the Heisenberg term. This procedure accounts for direct interatomic exchange as well as RKKY interaction via the conductivity band [11,12]. The total Hamiltonian then takes the form

$$H = H_{CS} + H_H, \tag{2}$$

where

$$H_H = \sum_{\langle ij \rangle} \Lambda_{ij} \mathbf{S}_i \mathbf{S}_j. \tag{3}$$

In compact Cr trimers, the value of parameter Λ_{ij} is determined mainly by the direct antiferromagnetic (AF) exchange. *Ab initio* calculations [10,13] of small free-standing Cr clusters demonstrate that this interaction has an order of eV, whereas estimation of RKKY coupling energy gives values less than a millivolt [5].

We start by investigating this model (2) for a compact symmetric trimer. In this case, all Λ_{ij} in (3) are equal: $\Lambda_{ij} = \Lambda$. Let us create a set of Yosida trial wave functions [14]

$$\hat{P}_j |0\rangle = \sum_{\mathbf{k}} \nu_{\mathbf{k}} e^{-i\mathbf{k}\mathbf{R}_j} (c^\dagger_{\mathbf{k}\uparrow} n_{dj\downarrow} - c^\dagger_{\mathbf{k}\downarrow} n_{dj\uparrow}) |0\rangle, \tag{4}$$

where the initial wave function is formed by the unperturbed Fermi sea and a paramagnetic (equiprobable) state of three localized spins $|0\rangle = (1/\sqrt{6}) \sum_{\sigma_1,\sigma_2,\sigma_3} |\sigma_1 \sigma_2 \sigma_3\rangle$; $n_{dj\sigma} = d^\dagger_{j\sigma} d_{j\sigma}$. Parameters $\nu_{\mathbf{k}}$ are real numbers ($\sum_{\mathbf{k}} \nu^2_{\mathbf{k}} = 1$), which must be determined via a variational procedure. The operator $\hat{P}_j$ adds to the system an additional conduction electron bonded to the localized spin,

so that $\hat{P}_j |0\rangle$ represents the singlet Kondo state on site j. These operators generate a subspace of trial wave functions $\hat{P}_1 |\sigma_1 \sigma_2 \sigma_3\rangle = |b_1 \sigma_2 \sigma_3\rangle$, $\hat{P}_2 |\sigma_1 \sigma_2 \sigma_3\rangle = |\sigma_1 b_2 \sigma_3\rangle$, and $\hat{P}_3 |\sigma_1 \sigma_2 \sigma_3\rangle = |\sigma_1 \sigma_2 b_3\rangle$.

In the same manner, we create a subspace of states with two (e.g., $\hat{P}_1 \hat{P}_2 |\sigma_1 \sigma_2 \sigma_3\rangle = |b_1 b_2 \sigma_3\rangle$) and three ($|b_1 b_2 b_3\rangle$) Kondo singlets. The last one is the ground state of the trimer in the limit of large distances between adatoms. Note that Hamiltonian (2) does not mix the different subspaces.

We consider below the subspace with only one Kondo singlet to construct the ground state of a compact trimer. The states with two and three singlets have no contribution from the Heisenberg term (3), and thus for sufficiently large Λ they have higher total energy. Therefore they can be neglected. The two unscreened spins may form either three triplet or one singlet states. We omit the triplets since in the case of AF exchange ($\Lambda > 0$) they have much higher energy. As a result, the following three singlet states remain:

$$|b_1\rangle = \frac{1}{\sqrt{2}} (|b_1 \uparrow\downarrow\rangle - |b_1 \downarrow\uparrow\rangle),$$

$$|b_2\rangle = \frac{1}{\sqrt{2}} (|\uparrow b_2 \downarrow\rangle - |\downarrow b_2 \uparrow\rangle), \tag{5}$$

$$|b_3\rangle = \frac{1}{\sqrt{2}} (|\uparrow\downarrow b_3\rangle - |\downarrow\uparrow b_3\rangle).$$

In the subspace of these vectors, the Hamiltonian (3) gives a constant contribution to the total energy $E_H = -3\Lambda/4$. Note that exactly the same energy E_H corresponds to the ground state with three unscreened spins due to magnetic frustrations in the equilateral trimer.

We assume the Fermi sea to be isotropic. Then the interaction between adatoms does not depend on the direction $\mathbf{R}_{ij}$ in the surface plane. The Hamiltonian (1) has the general matrix form

$$H_{CS} = \begin{pmatrix} A & B & -B \\ B & A & B \\ -B & B & A \end{pmatrix} \tag{6}$$

in the representation (5). The diagonal elements correspond to the Kondo singlet localized on each atom of the trimer whereas the nondiagonal terms describe transitions of the Kondo state from one adatom to another. The eigenvectors of the matrix (6) are

$$|1\rangle = \frac{1}{\sqrt{3}} (|b_1\rangle - |b_2\rangle + |b_3\rangle),$$

$$|2\rangle = \frac{1}{\sqrt{2}} (-|b_1\rangle + |b_3\rangle), \tag{7}$$

$$|3\rangle = \frac{1}{\sqrt{2}} (|b_1\rangle + |b_2\rangle).$$

The eigenvalues of the second and third vectors are degenerate. A graphic representation of state $|1\rangle$ is shown in Fig. 1. The Schrödinger equation for this state takes the form
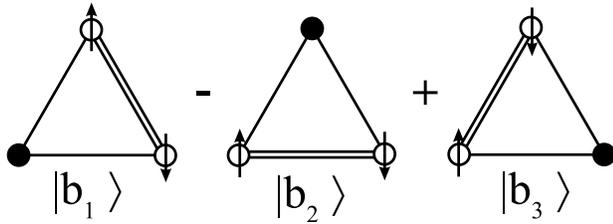
FIG. 1. Representation of the ground state of a compact trimer. The black circles are Kondo singlets while double lines denote the singlet states of two localized spins.

$$\nu_k(\varepsilon_k - E) = \frac{3\Gamma}{2L} \sum_{\mathbf{k}'} \nu_{k'}(1 + 2|Y_{20}|^2 e^{i\mathbf{k}'\mathbf{R}}), \qquad (8)$$

where $\nu_{\mathbf{k}} = \nu_k Y_{20}(\Omega_{\mathbf{k}})$, $\mathbf{R}$ is a vector in the surface plane, and $|\mathbf{R}|$ is the distance between adatoms in the trimer.

Then we pass from a summation to an integration over spherical coordinates in Eq. (8):

$$\frac{1}{L}\sum_{\mathbf{k}} \rightarrow \frac{3}{4\pi k_D^3} \int_{k_F}^{k_D} k^2 dk \int_0^\pi \sin(\vartheta)d\vartheta \int_0^{2\pi} d\varphi, \qquad (9)$$

where k_F and k_D are the Fermi vector and the cutoff vector, respectively. Expanding the plane wave $\exp[i\mathbf{k}'\mathbf{R}]$ into the spherical harmonics, we separate the integration over the radial and angular variables. To estimate the integral, we retain the first term of the series. Finally, the eigenvalue corresponding to the state is

$$E_1 = -\varepsilon_0 \exp\left(-\frac{s}{1+2t}\right), \qquad (10)$$

where $\varepsilon_0 = 4\varepsilon_F(k_D - k_F)/(k_D + k_F)$, $s = 2/[3\Gamma\rho(\varepsilon_F)]$, ε_F is the Fermi energy, $\rho(\varepsilon_F)$ is the density of states (DOS) at the Fermi level, and $t = \sin(Rk_F)/(Rk_F)$. It is convenient to calculate the energy from the ground state level of the Hamiltonian (3). Then Eq. (10) gives the true energy of the state. In the same manner, we obtain the eigenvalue corresponding to the vector $|2\rangle$ ($|3\rangle$)

$$E_{2(3)} = -\varepsilon_0 \exp\left(-\frac{s}{1-t}\right). \qquad (11)$$

The energy of the Kondo singlet of a monomer can be obtained from Eq. (10) or Eq. (11) if $t = 0$. Depending on the sign of $\sin(k_F R)$, states $|1\rangle$ or $|2\rangle$ ($|3\rangle$) become the ground one. Note that for all $t \neq 0$ the ground state energy for the trimer proves to be lower than for a single adatom. For small distances R (i.e., for the compact trimer) $t > 0$ and the state $|1\rangle$ determines the Kondo temperature. Similar solutions can be obtained for a dimer [12] but in this case the loss of the Heisenberg energy suppresses the transition to the Kondo state.

Let us consider an isosceles trimer. Shifting the second adatom off the symmetric position (see the inset of Fig. 2) leads to nonequal distances between adatoms and therefore to distinct exchange constants Λ_{ij} ($\Lambda_{12} = \Lambda_{23} = \Lambda_l$, $\Lambda_{23} = \Lambda_s$, $\Lambda_l < \Lambda_s$). Since the exchange interaction in a
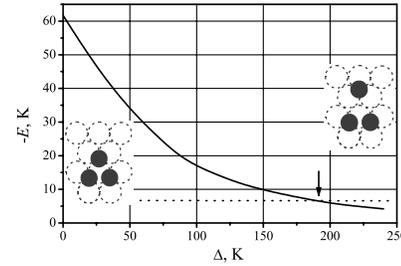

FIG. 2. The Kondo energy of the isosceles trimer vs Δ. The arrow shows the point where $E_K = -6$ K. The insets show a symmetric trimer (on the left, $\Delta = 0$) and an isosceles trimer (on the right). The black circles are the Cr adatoms placed on the closed-packed surface background (dashed circles).

Cr-Cr pair strongly depends on separation, we assume that, for small shifts, $\sin(k_F R)/(k_F R)$ can be considered to be constant and only the variation of the exchange constant Λ_{ij} is responsible for modifying the trimer's behavior. We look for the ground state of an isosceles trimer in the form

$$|G\rangle = \frac{1}{\sqrt{2\alpha^2 + \beta^2}}(\alpha|b_1\rangle - \beta|b_2\rangle + \alpha|b_3\rangle), \qquad (12)$$

where the coefficients α and β depend on the interatomic distances. For the equilateral compact trimer [$\sin(k_F R) > 0$] $\alpha = \beta = 1$, whereas when $R_{12} = R_{23} \gg R_{13}$, $\alpha = 0$ and $\beta = 1$. Since the positions of atoms 2 and 1 (3) are nonequivalent, the coefficients $\nu_{\mathbf{k}}$ in the expression for the operator $\hat{P}_i$ depend on the position of adatom j in the isosceles trimer ($\nu_{1\mathbf{k}} = \nu_{3\mathbf{k}} = \nu_{\alpha\mathbf{k}}$, $\nu_{2\mathbf{k}} = \nu_{\beta\mathbf{k}}$, $\nu_{\alpha\mathbf{k}} \neq \nu_{\beta\mathbf{k}}$). The energy associated with the Heisenberg term (3) in the ground state, $E_H = -3\Lambda_s/4$, is included in the zero energy level, as above. The Schrödinger equation for the state $|G\rangle$ is then separated into two equations for the coefficients $\alpha\nu_{\alpha\mathbf{k}}$ and $\beta\nu_{\beta\mathbf{k}}$:

$$(\varepsilon_k + \Delta - E)\alpha\nu_{\alpha k}$$
$$= \frac{3\Gamma}{2L}\sum_{\mathbf{k}'}(\alpha\nu_{\alpha k'} + e^{i\mathbf{k}'\mathbf{R}}[\alpha\nu_{\alpha k'} + \beta\nu_{\beta k'}]),$$

$$(\varepsilon_k - E)\beta\nu_{\beta k} = \frac{3\Gamma}{2L}\sum_{\mathbf{k}'}(\beta\nu_{\beta k'} + 2e^{i\mathbf{k}'\mathbf{R}}\alpha\nu_{\alpha k'}). \qquad (13)$$

where $\Delta = \frac{3}{4}(\Lambda_s - \Lambda_l) > 0$. After replacement of the summation by an integration, the system of equations in (13) can be reduced to

$$E = -\varepsilon_0 \exp\left[-\frac{s(1-tx)}{1+t-2t^2}\right] + \Delta,$$
$$E = -\varepsilon_0 \exp\left[-\frac{s(tx+x-2t)}{x(1+t-2t^2)}\right]. \qquad (14)$$

Here ε_0 and t are the same as in Eq. (10) and $x = \beta(\varepsilon_F - E)/[(\varepsilon_F + \Delta - E)\alpha]$. This system of equations can be easily solved numerically with respect to the unknown variables E and x.

We can now make an estimation of the ground state energy, which determines the temperature of transition to the Kondo state. First, we assume the values of parameters for bulk Au $\varepsilon_0 \approx \varepsilon_F \approx 64\,000$ K, $k_F \approx 10^8$ cm^{-1} [7], which yield $t = 0.08$. The value of parameter s is chosen to ensure that the Kondo temperature for a single Cr adatom is below the experimental temperature (7 K), since no Kondo resonance was detected for Cr monomers in experiment [6]. A simple estimate using Eq. (10) shows that the Kondo temperature decreases from 2.9 to 0.1 K when s is increased from 10 to 13. The nondiagonal terms of (6) cause enlargement of the Kondo energy in the trimer. However, even if we choose $T_K = 2.9$ K ($s = 10$) for a single adatom, we obtain only $T_K = 12.1$ K for the trimer. This value is still much lower than the experimental one for a trimer (≈ 50 K) [6]. Therefore, for a quantitative explanation of the experiment, we must include the dispersion of itinerant surface states of the metal substrate.

It is well known that delocalized 2D surface states exist on the close-packed faces of the noble metals due to the gap along the Γ-L direction in the bulk metal [e.g., the Au(111) surface [15]]. STM techniques have provided a direct observation of perturbations in these surface states caused by adatoms. Therefore it is natural to assume that the interaction of the atomic states and the 2D surface states has some influence on the magnetic behavior of a cluster. The Fermi vector for these electrons proves to be essentially smaller than for bulk ones and therefore we can wait that the value t in (10) will be close to 1 for typical distances in the compact trimer. It has to increase the Kondo temperature. To confirm this quantitatively we apply the same model for itinerant 2D electrons that we did for bulklike electrons. Then in the Hamiltonian (1) the interaction constant should be replaced by $\Gamma_{\mathbf{k}\mathbf{k}'} = \Gamma \exp[im(\varphi_{\mathbf{k}'} - \varphi_{\mathbf{k}})]$, where m is the projection of the orbital moment on a z axis perpendicular to the surface; $\varphi_{\mathbf{k}'}$ and $\varphi_{\mathbf{k}}$ are the angles in cylindrical coordinates. In Eqs. (8) and (13), we transfer from a summation to an integration. After calculations performed exactly in the same way as above, we obtain Eqs. (10), (11), and (14), except that preexponential factor ε_0 and the function t are replaced, respectively, by $\varepsilon_0 = \varepsilon_D - \varepsilon_F$ and $t = J_0(k_F R)$, where J_0 is the zeroth order Bessel function.

The dispersion law for surface state electrons can be estimated from the experimental data [15]: At 4 K, the Au(111) surface state dispersion is parabolic, with an effective mass ratio 0.26 and a band edge 0.52 eV below the Fermi energy. It gives $\varepsilon_0 \approx \varepsilon_F \approx 6000$ K and $k_F \approx 2 \times 10^7$ cm^{-1} ($t = 0.92$). Using $s = 11$, we obtain $T_K = 0.1$ K for a single adatom. The Kondo energy for a symmetric trimer then proves to be 125 K. The increase of the Kondo energy for the trimer with respect to the monomer is 3 orders of magnitude. It is worth emphasizing again that the drastic enhancement of the Kondo state energy stems from the fact that, for surface states (in contrast to the bulk states), the natural unit length k_F^{-1} is of the same order as interatomic distances in trimer.

Let us consider now the situation for an isosceles Cr trimer. The temperature of transition to the Kondo state can be obtained from the solution of the equations in (14). The dependence $E(\Delta)$ for the surface electrons is shown in Fig. 2. It is clear that a small difference between Λ_l and Λ_s (Λ are of the order of 1 eV, i.e., 10^4 K) causes a strong suppression of the Kondo temperature. This explains the high sensitivity of the Kondo temperature to trimer geometry which was found in STM experiments [6].

The model discussed above is based on the assumption that a Cr adatom can be treated as a doubly degenerate state. In fact, a free Cr atom has a half-filled $3d$ shell with the total spin $S = 5/2$ and the orbital moment $L = 0$. The degeneracy of free $3d$ levels is partially lifted by the Au(111) cleavage. The interaction of an adatom with two other adatoms in a trimer acts as a crystal field with a low symmetry and totally lifts the orbital degeneracy. Thus, the model presented above can be appropriately generalized to multielectron shells.

In summary, we have developed a variational theory for the description of the Kondo resonance in small supported clusters. The Kondo temperature for an equilateral Cr trimer was found to be always higher than for a single Cr adatom. For compact trimers this difference can be quite large. The Kondo state also proved to be very sensitive to trimer geometry and can be suppressed by a transition from an equilateral to an isosceles shape.

We gratefully acknowledge M. F. Crommie for very useful discussions.

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*Electronic address: kudasov@ntc1.vniief.ru
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