Kondo Box: A Magnetic Impurity in an Ultrasmall Metallic Grain

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(Received 30 September 1998)

We study the Kondo effect generated by a single magnetic impurity embedded in an ultrasmall metallic grain, to be called a "Kondo box." We find that the Kondo resonance is strongly affected when the mean level spacing in the grain becomes larger than the Kondo temperature, in a way that depends on the parity of the number of electrons on the grain. We show that the single-electron tunneling conductance through such a grain features Kondo-induced Fano-type resonances of measurable size, with an anomalous dependence on temperature and level spacing. [S0031-9007(99)08630-5]

PACS numbers: 72.15.Qm, 71.27.+a, 73.20.Dx, 73.23.Hk

What happens to the Kondo effect when a metal sample containing magnetic impurities is made so small that its conduction electron spectrum becomes discrete with a nonzero mean level spacing Δ? One expects the Kondo resonance at the Fermi energy ε_F to be affected when $\Delta \simeq T_K$, the bulk Kondo temperature, since a fully developed resonance requires a finite density of states (DOS) near ε_F, and Δ acts as a low-energy cutoff for the spin scattering amplitude.

To achieve $\Delta \gtrsim T_K$, the sample would have to be an ultrasmall metallic grain containing magnetic impurities, to be called a "Kondo box": For example, for a metal grain of volume $\mathcal{V} = (15\text{ nm})^3 - (3\text{ nm})^3$ and $k_F \simeq 1$ Å^{-1}, the free-electron estimate $\Delta = 1/N_0 \simeq 2\pi^2\hbar^2/(mk_F\mathcal{V})$, with N_0 the bulk DOS near ε_F, gives $\Delta \simeq 0.5$–60 K, which sweeps a range including many typical Kondo temperatures. The discrete DOS of an *individual* grain of this size can be measured directly using single-electron tunneling (SET) spectroscopy [1,2], as shown by Black, Ralph, and Tinkham [1] in their studies of how a large level spacing affects superconductivity. Analogous experiments on a Kondo box should be able to probe how a large Δ ($\simeq T_K$) affects Kondo physics.

In this Letter, we study this question theoretically. We find (i) that the Kondo resonance splits up into a series of subpeaks corresponding to the discrete box levels; (ii) that its signature in the SET conductance through the grain consists of Fano-like line shapes with an anomalous temperature dependence, estimated to be of measurable size; (iii) an even/odd effect: If the total number of electrons on the grain (i.e., delocalized conduction electrons plus one localized impurity electron) is odd, the weight of the Kondo resonance decreases more strongly with increasing Δ and T than if it is even.

The model.—For the impurity concentrations of 0.01% to 0.001% that yield a detectable Kondo effect in bulk alloys, an ultrasmall grain of typically 10^4–10^5 atoms will contain only a single impurity, so that interimpurity interactions need not be considered. We thus begin by studying the local dynamics of a single impurity in an isolated Kondo box, for which we adopt the (infinite U) Anderson model with a discrete conduction spectrum, in the slave-boson representation:

$$H = H_0 + \varepsilon_d \sum_\sigma f_\sigma^\dagger f_\sigma + v \sum_{j,\sigma} (c_{j\sigma}^\dagger b^\dagger f_\sigma + \text{H.c.}), \quad (1)$$

where $H_0 = \sum_{j,\sigma} \varepsilon_j c_{j\sigma}^\dagger c_{j\sigma}$. Here, σ denotes spin and the $c_{j\sigma}^\dagger$ create conduction electrons in the discrete, delocalized eigenstates $|j\sigma\rangle$ of the "free" system (i.e., without impurity). Their energies, measured relative to the chemical potential μ, are taken uniformly spaced for simplicity: $\varepsilon_j = j\Delta + \bar{\varepsilon}_0 - \mu$. As in [3], we follow the so-called orthodox model and assume that the ε_j's include all effects of Coulomb interactions involving delocalized electrons, up to an overall constant, the charging energy E_C. The localized level of the magnetic impurity has bare energy ε_d far below ε_F, and is represented in terms of auxiliary fermion and boson operators as $d_\sigma^\dagger = f_\sigma^\dagger b$, supplemented by the constraint $\sum_\sigma f_\sigma^\dagger f_\sigma + b^\dagger b = 1$ [4], which implements the limit $U \to \infty$ for the Coulomb repulsion U between two electrons on the d level. Its hybridization matrix element v with the conduction band is an overlap integral between a localized and a delocalized wave function, and, due to the normalization of the latter, scales as $\mathcal{V}^{-1/2}$. Thus the effective width of the d level, $\Gamma = \pi v^2/\Delta$, is volume independent, as is the bulk Kondo temperature, $T_K = \sqrt{2\Gamma D/\pi}\,\exp(-\pi\varepsilon_d/2\Gamma)$, where D is a high energy band cutoff. To distinguish, within the grand canonical formalism, grains for which the total number of electrons is even or odd, we choose μ either on ($\mu = \bar{\varepsilon}_0$) or halfway between two ($\mu = \bar{\varepsilon}_0 + \Delta/2$) single-particle levels, respectively [3].

NCA approach.—We calculated the spectral density $A_{d\sigma}(\omega)$ of the impurity Green's function $G_{d\sigma}(t) = -i\theta(t)\langle\{d_\sigma(t), d_\sigma^\dagger(0)\}\rangle$ using the noncrossing approximation (NCA) [5]. For a continuous conduction band, the NCA is known to be reliable down to energies of $0.1T_K$ or less, producing spurious singularities only for T below this scale [6,7]. Since these are cut off by the level spacing Δ in the present case, we expect the

NCA to be semiquantitatively accurate over the entire parameter range studied here (T and Δ between $0.1T_K$ and $5T_K$). Denoting the retarded auxiliary fermion and boson propagators by $G_{f\sigma}(\omega) = [\omega - \varepsilon_d - \Sigma_{f\sigma}(\omega)]^{-1}$, $G_b(\omega) = [\omega - \Sigma_b(\omega)]^{-1}$, respectively, the self-consistent NCA equations read

$$\Sigma_{f\sigma}(\omega) = \Gamma \int \frac{d\varepsilon}{\pi} [1 - f(\varepsilon)] A^{(0)}_{c\sigma}(\varepsilon) G_b(\omega - \varepsilon), \quad (2)$$

$$\Sigma_b(\omega) = \Gamma \sum_\sigma \int \frac{d\varepsilon}{\pi} f(\varepsilon) A^{(0)}_{c\sigma}(\varepsilon) G_{f\sigma}(\omega + \varepsilon), \quad (3)$$

where $f(\omega) = 1/[\exp(\omega/T) + 1]$. The finite grain size enters through the discreteness of the (dimensionless) single-particle spectral density of the box *without* impurity, $A^{(0)}_{c\sigma}(\omega) = \Delta \sum_j \delta(\omega - \epsilon_j)$. (We checked that broadening the Dirac δ's by a width $\gamma \lesssim 0.1T_K$ essentially does not change the $\gamma = 0$ results shown here.) In terms of the auxiliary particle spectral functions $A^+_{f,b} = -\frac{1}{\pi} \operatorname{Im} G_{f,b}$, $A_{d\sigma}(\omega)$ is given by (for details, see [7], Eq. (24), [8])

$$A_{d\sigma}(\omega) = \int d\varepsilon [e^{-\beta\varepsilon} + e^{-\beta(\varepsilon - \omega)}] A^+_{f\sigma}(\varepsilon) A^+_b(\varepsilon - \omega). \quad (4)$$

Numerical results.—The results obtained for $A_{d\sigma}(\omega)$ by numerically solving the NCA Eqs. (2) to (4) for various T and Δ are summarized in Figs. 1 and 2. (We have checked that the equation-of-motion method [9] yields qualitatively similar results for all quantities discussed below.) For $\Delta \ll T$, the shape of the Kondo resonance is indistinguishable from the bulk case ($\Delta \to 0$). When Δ is increased well beyond T, however, it splits up into a set of individual subpeaks, each of which we found to sharpen without saturation as T is decreased down to the lowest temperatures for which our numerics were stable ($T \simeq 0.2\Delta$). Indeed, at $T = 0$ *each* peak of $A_{d\sigma}(\omega)$ should have zero width, according to the exact Lehmann representation. The latter also requires many additional zero-width "sublines" to appear for $T > 0$, with exponentially small weights if $\Delta/T > 1$. The NCA is unable to resolve these (since self-consistency conditions tend to push Green's function poles off the real axis, thereby broadening spectral peaks), but given the limited resolution of measured grain spectra [1], our goal here is merely to study the *dominant* spectral features.

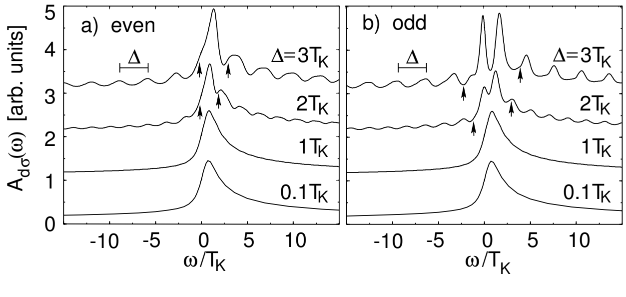

FIG. 1. Impurity spectral function $A_{d\sigma}(\omega)$ for various values of Δ at $T = 0.5T_K$; (a) even and (b) odd total number of electrons. The individual curves are offset by one unit each.

Despite developing subpeaks, the Kondo resonance retains its main feature, namely significant spectral weight within a few T_K around the Fermi energy, up to the largest ratios of $\Delta/\max(T, T_K)$ ($\simeq 5$) we considered. This implies that the Kondo correlations induced by the spin-flip transitions between the d level and the lowest-lying unoccupied j levels persist up to remarkably large values of $\Delta/\max(T, T_K)$ [10]. However, they do weaken systematically with increasing Δ, as can see in the inset of Fig. 2, which shows the average peak height of the Kondo resonance (which quantifies the "strength" of the Kondo correlations) as a function of Δ at fixed T: The peak height drops logarithmically with increasing Δ once Δ becomes larger than about T. Conversely, at fixed Δ, it drops logarithmically with increasing T once T becomes larger than about 0.5Δ (main part of Fig. 2), thus reproducing the familiar bulk behavior. Qualitatively, these features are readily understood in perturbation theory, where the logarithmic divergence of the spin-flip amplitude, $t(\omega) \propto \sum_{\varepsilon_j \neq \omega} \frac{f(\varepsilon_j)}{\omega - \varepsilon_j}$, is cut off by either T or Δ, whichever is largest.

Parity effects.—For $\Delta \gg T$, the even and odd spectral functions $A_{d\sigma}$ in Fig. 1 differ strikingly: The former has a single central main peak, whereas the latter has two main peaks of roughly equal weight. This can be understood as follows: For an even grain, spin-flip transitions lower the energy by roughly T_K by binding the d electron and the conduction electrons into a Kondo singlet, in which the topmost, *singly* occupied j level of the free Fermi sea carries the dominant weight, hence, the single

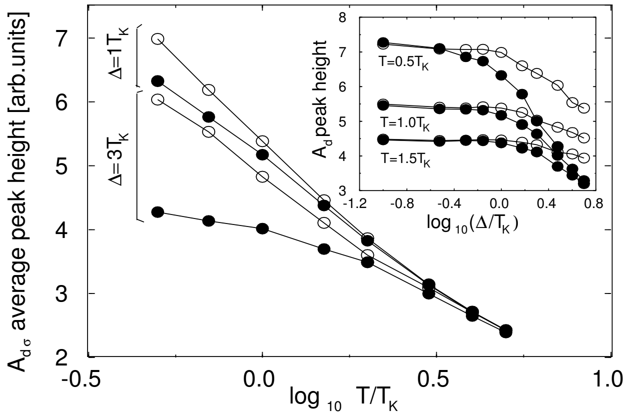

FIG. 2. Even/odd dependence of the average peak height of the Kondo resonance, as a function of T/T_K. For an even box (○), we averaged $A_{d\sigma}$ over a range Δ centered on its central subpeak, for an odd box (●) over a range 2Δ centered on its central two subpeaks (as indicated by arrows in Fig. 1). The inset shows the same quantity as a function of Δ/T_K. Numerical uncertainties are smaller than the symbol sizes.

dominant peak in $A_{d\sigma}$. For an odd grain, in contrast, the free Fermi sea's topmost j level is *doubly* occupied, blocking energy-lowering spin-flip transitions. To allow the latter to occur, these topmost two electrons are redistributed with roughly equal weights between this and the next-higher-lying level, causing two main peaks in $A_{d\sigma}$ and reducing the net energy gain from T_K by an amount of order Δ. This energy penalty intrinsically weakens Kondo correlations in odd relative to even grains; indeed, the average $A_{d\sigma}$ peak heights in Fig. 2 are systematically lower in odd than in even grains, and more so the larger Δ and the smaller T.

SET conductance.—The above physics should show up in SET spectroscopy experiments: When an ultrasmall grain is connected via tunnel junctions to left (L) and right (R) leads [11] and if the tunneling current through the grain is sufficiently small (so that it only probes but does not disturb the physics on the grain), the tunneling conductance $G(V)$ as function of the transport voltage V has been demonstrated [1] to reflect the grain's discrete, equilibrium conduction electron DOS. Such measurements are parity sensitive [1] even though a nonzero current requires parity fluctuations, since the latter can be minimized by exploiting the huge charging energies ($E_c > 50$ K) of the ultrasmall grain. To calculate the SET current, we describe tunneling between grain and leads by $H_t = \sum_{kj\sigma\alpha}(u^{\alpha}_{kj\sigma} c^{\dagger}_{k\sigma\alpha} c_{j\sigma} + \text{H.c.})$, where $c^{\dagger}_{k\sigma\alpha}$ creates a spin σ electron in channel k of lead $\alpha \in \{L, R\}$. Neglecting nonequilibrium effects in the grain, the tunneling current has the Landauer-Büttiker form [12]:

$$I(V) = \frac{e}{\hbar} \int d\omega\, F_V(\omega) \sum_{j\sigma} \left[\frac{\gamma^L \gamma^R}{\gamma^L + \gamma^R} \right]_{j\sigma} A_{c,j\sigma}(\omega), \tag{5}$$

where $F_V(\omega) = f(\omega - eV/2) - f(\omega + eV/2)$, $A_{c,j\sigma}$ is the spectral density of $G_{c,j\sigma}(t) = -i\theta(t)\langle\{c_{j\sigma}(t), c^{\dagger}_{j\sigma}(0)\}\rangle$, and $\gamma^{\alpha}_{j\sigma} = 2\pi \sum_k |u^{\alpha}_{kj\sigma}|^2$ [13]. Neglecting the $\alpha j\sigma$ dependence of γ, the current thus is governed by the conduction electron DOS, $A_c(\omega) = \sum_{j\sigma} A_{c,j\sigma}(\omega)$. Exploiting a Dyson equation for $G_{c,j\sigma}$, it has the form

$$A_c(\omega) = -\frac{1}{\pi} \sum_{j\sigma} \times \mathrm{Im}[G^{(0)}_{c,j\sigma}(\omega) + v^2 [G^{(0)}_{c,j\sigma}(\omega)]^2 G_{d\sigma}(\omega)],$$

where $G^{(0)}_{c,j\sigma} = 1/(\omega - \varepsilon_j + i0^+)$ is the free conduction electron Green's function [14], and the corresponding Kondo contribution to the conductance $G(V) = dI(V)/dV = G_0(V) + \delta G(V)$ is

$$\delta G(V) = -\frac{e^2}{\hbar} \gamma \frac{\Gamma}{\pi} \Delta \sum_{j,\sigma} \mathcal{P}\!\!\int d\omega\, A_{d\sigma}(\omega) \times \left[\frac{\tilde{F}_V(\omega) - \tilde{F}_V(\varepsilon_j)}{(\omega - \varepsilon_j)^2} - \frac{d\tilde{F}_V(\omega)/d\omega}{\omega - \varepsilon_j} \right], \tag{6}$$

with $\tilde{F}_V(\omega) = -\frac{d}{d\omega}[f(\omega - eV/2) + f(\omega + eV/2)]/2$. Even though Kondo physics appears only in the subleading contributions to $A_c(\omega)$ and $G(V)$, these are proportional to $v^2 = \Gamma\Delta/\pi$ and thus *grow* with decreasing grain size.

$G_0(V)$, $\delta G(V)$, and $G(V)$ are shown in Fig. 3. G_0 and δG, derived from the first and second terms of $A_c(\omega)$, are "out of phase," because $\mathrm{Im}\, G^{(0)}_{c,j\sigma}(\omega) \gg \mathrm{Re}\, G^{(0)}_{c,j\sigma}(\omega)$ near the peaks of $G^{(0)}_{c,j\sigma}(\omega)$ (by Kramers-Kroenig). Moreover, δG and G have rather irregular structures and line shapes, due to *interference* between $G_{d\sigma}$ and $[G^{(0)}_{c,j\sigma}]^2$ in A_c, and correspondingly between $A_{d\sigma}$ and the bracketed factor in (6) for $\delta G(V)$. This interference is reminiscent of a Fano resonance [15], which likewise arises from the interference between a resonance and the conduction electron DOS. Incidentally, Fano-like interference has been observed in scanning tunneling microscopy spectroscopy of a single Kondo ion on a metal surface [16], for which the conduction electron DOS is flat. In contrast, for an ultrasmall grain it consists of discrete peaks, reflected in the last factor in Eq. (6). This leads to a much more complex interference pattern, which does not directly mirror the specific peak structure of $A_{d\sigma}(\omega)$ discussed above.

Nevertheless, $G(V)$ does bear observable traces of the Kondo effect, in that *the interference pattern shows a distinct, anomalous T dependence,* due to that of the Kondo resonance. In particular, the weights W_j under the individual peaks of $G(V)$ become T dependent. (In contrast, the weight W_0 under an individual peak of the bare conductance $G_0(V)$ is T independent, since the T dependence of the peak shapes of G_0 is determined solely by $df(\omega)/d\omega$.) This is illustrated in Fig. 4, which shows the T dependence of the weights W_1 and W_2 of the first and second conductance peaks (counted relative to

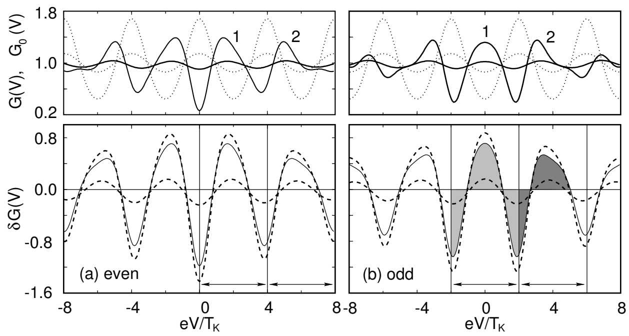

FIG. 3. Differential conductance of (a) an even and (b) an odd Kondo box for $\Delta = 4T_K$. Dotted, dashed, and bold solid lines give, respectively, the bare conductance $G_0(V)$, the Kondo contribution $\delta G(V)$, and the total conductance $G_0 + \delta G$. The curves with larger (smaller) amplitudes correspond to $T = 0.6T_K$ ($1T_K$); all are normalized such that the average of the bare conductance $\overline{G}_0(V) = 1$. Thin solid lines in the lower panels show $\delta G(V, T = 0.6T_K) - \delta G(V, T = 1T_K)$; i.e., the shaded areas (including signs) give the corresponding *change* of the weights W_1, W_2 of the first and second conductance peaks, as T is lowered. This change is negative for W_1 and positive for W_2 (see Fig. 4).

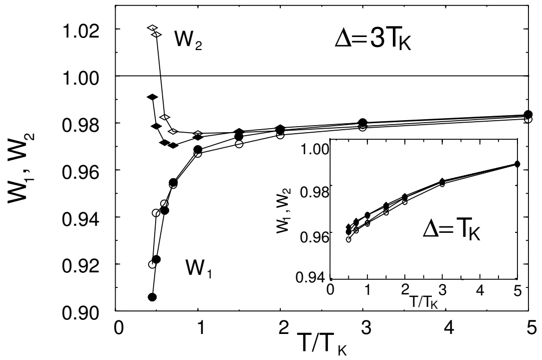

FIG. 4. Anomalous temperature dependence of the weights W_1 (circles) and W_2 (diamonds) of the first two conductance peaks of an even grain (○, ◇) and an odd grain (●, ◆), for $\Delta = 3T_K$ and $\Delta = T_K$ (inset). We calculated the weights under $G(V)$ over a fixed range $V = \Delta$ between successive maxima of $G_0(V)$ (see arrows in Fig. 3).

$V = 0$ and labeled 1,2 in Fig. 3): When T decreases at fixed $\Delta = T_K$, both W_1 and W_2 decrease, while at fixed $\Delta = 3T_K$, W_1 decreases whereas W_2 increases. The fact that the weights can either increase or decrease with decreasing T results from the constructive or destructive Fano-like interference effects discussed above. Moreover, at the larger value for Δ, both W_1 and W_2 develop a *parity effect in the strength of their T dependence.*

The Kondo-induced T dependence in peak weights in Fig. 4 should be strong enough to be experimentally detectable [1]. For, e.g., an Fe impurity in an even Cu grain of size $(3\text{ nm})^3$ ($\Delta = 30$ K, $T_K \simeq 10$ K), cooling from $T = 2T_K$ to $0.5T_K$ should change W_1 by $\simeq 7\%$. (We expect W_1 to change some more as T is lowered further, though our numerics become unreliable in this regime.)

Coherence length.—The condition $\Delta > T_K$ implies a relation between sample volume and the much-discussed spin coherence length $\xi_K = 2\pi v_F/T_K$, namely, (in 3D) $\mathcal{V} < \pi\xi_K/k_F^2$. Note that this relation involves both the small length scale $1/k_F$ and the sample's *volume,* but not the smallest of its linear dimensions, say L. This implies that the length scale below which purely finite-size induced modifications of Kondo physics can be expected is *not* set by ξ_K alone [17], and indeed may be considerably smaller than ξ_K. This is why such modifications were not found in the numerous recent experiments having $L \lesssim \xi_K$ for one or two of the sample's dimensions [18,19].

In conclusion, we have analyzed the Kondo effect in an ultrasmall metallic grain containing a single magnetic ion. The presence of a new energy scale in the system, the mean level spacing Δ, leads to a rich physical behavior when $\Delta \sim T_K$, including a distinct even/odd effect. Our NCA calculations, which give a semiquantitatively reliable estimate of the size of the effects to be expected in future experiments, predict that the SET conductance through such a grain has a Kondo-induced anomalous T dependence of up to 10%. Since the effects discussed in this work result, above all, from the discrete density of states near ε_F, they should be generic for ultrasmall grains, i.e., robust against including randomness in the model, such as j-dependent level spacings Δ_j and hybridization matrix elements v_j, or resolving the substructure in $A_{d\sigma}(\omega)$ that the NCA smears out.

We are grateful to V. Ambegaokar, S. Böcker, F. Braun, T. Costi, C. Dobler, P. Fulde, A. Garg, D. Ralph, A. Rosch, G. Schön, N. Wingreen, P. Wölfle, and G. Zaránd for useful discussions. This work was started at an ISI Euroconference in Torino, and was supported by the DFG through SFB195.

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