Mixed-Valent Regime of the Two-Channel Anderson Impurity as a model for UBe_{13}

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We investigate the mixed-valent regime of a two-configuration Anderson impurity model for uranium ions, with separate quadrupolar and magnetic doublets. With a new Monte Carlo approach and the noncrossing approximation we find (i) a non-Fermi-liquid fixed point with two-channel Kondo model critical behavior, (ii) distinct energy scales for screening the low-lying and excited doublets; (iii) a semiquantitative explanation of magnetic-susceptibility data for $U_{1-x}Th_xBe_{13}$ assuming 60% − 70% quadrupolar doublet ground-state weight, supporting the quadrupolar-Kondo interpretation. [S0031-9007(98)07334-7]

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Since the 1950's, Landau's Fermi-liquid theory has shaped our understanding of the metallic state. Based on the notion of a one-to-one mapping between the low-lying excitations of the interacting system and that of the noninteracting electron gas, the theory provides a remarkably robust scenario for the low-temperature properties of interacting electron systems. It is against this outstanding success that a growing class of f-shell materials—predominantly Ce- and U-based alloys—received considerable attention in recent years. Characterized by a logarithmically divergent linear coefficient of specific heat and anomalous temperature dependences of the resistivity and susceptibility, these materials appear to depart from the conventional Fermi-liquid scenario [1], thus challenging our understanding of metallic behavior.

In this paper, we present results on the two-channel Anderson impurity model in the mixed-valent regime, motivated by the unusual nonlinear susceptibility data of the non-Fermi-liquid (NFL) alloy system $U_{1-x}Th_xBe_{13}$. The restricted Hilbert space of our model, a ground quadrupolar (non-Kramers) doublet in the $5f^2$ configuration and a ground magnetic (Kramers) doublet in the $5f^3$ configuration, renders it intractable to study by conventional Monte Carlo methods. We have developed a new Monte Carlo method based upon the mapping onto a Coulomb gas. We use this method to calibrate noncrossing approximation (NCA) results, which can then be extended to more extreme parameter regimes. We find that the model displays NFL physics characteristic of the two-channel Kondo model, even at the extreme mixed-valent limit when the two charge configurations are degenerate. We also find that two energy scales appear in the screening process away from the configurational degeneracy point. Using this model we are able to semiquantitatively explain the linear and nonlinear susceptibility data by assuming 60% − 70% ground-state weight for the quadrupolar doublet, with the Th doping inducing a higher $5f^2$ count, consistent with expectations from lattice constant data. We do not, however, explain the small energy scale for UBe_{13}, and anticipate that dynamical inclusion of excited crystal field (CEF) levels in the $5f^2$ configuration may remedy this problem.

A proposed scenario for the NFL physics of UBe_{13} involves the screening of uranium quadrupole moments in the $5f^2$ configuration by conduction orbital motion [2]. This quadrupolar Kondo effect can explain the enhanced specific heat and other data in this compound. In principle, though, the screened moment in the scenario of Ref. 2 can be either magnetic or quadrupolar, depending on which ionic charge configuration (U^{3+} or U^{4+}) is lower in energy. Which case is realized in UBe_{13} is still unresolved. While the nonlinear magnetic susceptibility [3] is suggestive of a magnetic trivalent state, the rather weak temperature dependence of the linear susceptibility is more consistent with a nonmagnetic tetravalent state. Recently, following experiments on the nonlinear susceptibility of $U_{0.9}Th_{0.1}Be_{13}$, Aliev *et al.* [4] suggested a different physical regime, in which strong quantum fluctuations drive the uranium ions to a mixed-valent state.

Here we explore the possibility of a mixed-valent state in the framework of the two-channel Anderson model [5], which consists of Γ_8 conduction electrons carrying both spin ($\sigma = \uparrow, \downarrow$) and quadrupolar ($\alpha = \pm$) quantum labels, hybridizing via a matrix element V with a local uranium ion. The latter is modeled by a Γ_3 quadrupolar doublet in the $5f^2$ configuration and a Γ_6 magnetic doublet in the $5f^3$ configuration, separated in energy by $\epsilon_f = E(5f^2) - E(5f^3)$. The corresponding Hamiltonian reads

$$\mathcal{H} = \sum_{k\alpha\sigma} \epsilon_k c^\dagger_{k\alpha\sigma} c_{k\alpha\sigma} + \epsilon_f \sum_{\alpha} |5f^2, \alpha\rangle\langle 5f^2, \alpha| + V \sum_{k\alpha\sigma} \{ c^\dagger_{k\alpha\sigma} |5f^2, -\alpha\rangle\langle 5f^3, \sigma| + \text{h.c.} \}, \quad (1)$$

where $c^\dagger_{k\alpha\sigma}$ creates a Γ_8 conduction electron with spin σ and quadrupolar moment α. This model may be applied to $U_{1-x}Th_xBe_{13}$ for temperatures above about half the Kondo scale, for which coherent lattice effects are small.

In the integer-valence limit, $\Gamma \equiv \pi \rho V^2 \ll |\epsilon_f|$ (ρ being the conduction-electron density of states at the Fermi level), Eq. (1) reduces to the two-channel Kondo Hamiltonian, [6], which is exactly solvable by a number of methods: Bethe ansatz [7], conformal field theory [8], and Abelian bosonization [9]. However, none of these solutions extend to the Hamiltonian of Eq. (1), where charge fluctuations are present. This model is also intractable to conventional determinantal quantum Monte Carlo.

To overcome the difficulties associated with the Hamiltonian of Eq. (1) we devised a new approach, based on (i) mapping the corresponding partition function onto a classical one-dimensional Coulomb gas, and (ii) sampling the latter gas using Monte Carlo techniques. This approach allows an accurate calculation of the low-temperature thermodynamics of the model deep into the mixed-valent regime, all the way from weak to strong coupling. It also enables the computation of the nonlinear susceptibility, which, due to the high-order correlation function involved, is typically inaccessible to determinantal quantum Monte Carlo methods. Below we outline our approach, starting with the mapping onto a Coulomb gas.

The formal connection between the Kondo effect and the statistical-mechanical problem of a one-dimensional Coulomb gas was first recognized for the Kondo Hamiltonian [10], and later extended to the one-channel Anderson model [11,12]. Here we generalize the mapping to the Hamiltonian of Eq. (1). The basic idea is to expand the partition function in powers of V, expressing it as a sum over all possible histories of the impurity. A history is a sequence of hopping events, or kinks, which preserve overall the impurity state and the occupation of each conduction-electron branch. Each history is represented by a sequence of impurity states, $\{\gamma_0, \dots, \gamma_n\}$, and a sequence of imaginary times, $\{\tau_1, \dots, \tau_n\}$, corresponding to the instances at which hopping events take place. Tracing over the conduction-electron degrees of freedom generates a long-range "Coulomb" interaction between the kinks within a given history. These couple through the four-component charges $\vec{\epsilon}_i = (\delta N_{\uparrow +}, \delta N_{\downarrow +}, \delta N_{\uparrow -}, \delta N_{\downarrow -})$, where $\delta N_{\sigma\alpha}$ is the change in occupancy of the σ, α conduction-electron branch due to the ith hopping event (i.e., the transition from state γ_{i-1} to state γ_i). Denoting the impurity-free partition function by Z_0, one has

$$\frac{Z}{Z_0} = \sum_{n=0}^{\infty} \left(\frac{\Gamma}{\pi D} \right)^{n/2} \sum_{\gamma_n = \gamma_0, \dots, \gamma_{n-1}} \delta_{\sum_i \vec{\epsilon}_i, 0} \int_0^{\beta} \frac{d\tau_n}{\tau_c} \dots \int_0^{\tau_2} \frac{d\tau_1}{\tau_c} \exp\left[\sum_{i>j=1}^{n} F(\tau_i - \tau_j) \vec{\epsilon}_i \cdot \vec{\epsilon}_j - \sum_{i=0}^{n} (\tau_{i+1} - \tau_i) E_{\gamma_i} \right], \tag{2}$$

where E_γ is the bare energy of the γ impurity state (zero for $5f^3$ and ϵ_f for $5f^2$); $F(\tau)$ is the interaction strength between kinks with time separation τ; and τ_0 and τ_{n+1} are equal to zero and β, respectively. At zero temperature, $F(\tau)$ reduces to $\ln(1 + |\tau|/\tau_c)$, where $D = 1/\tau_c$ plays the role of a bandwidth. At $T > 0$, the logarithm is replaced by a more complicated expression. The neutrality condition $\delta_{\sum_i \vec{\epsilon}_i, 0}$ selects only those histories that overall preserve the occupation of each conduction branch.

The impurity contribution to thermodynamic quantities can be computed directly from the Coulomb-gas representation of Eq. (2) using Monte Carlo techniques. This formulation has the crucial advantage of being free of any sign problem, as the different terms in Eq. (2) are all positive. Below we present our results for the mixed-valent regime.

We begin our discussion with the limit of strong valence fluctuations, $|\epsilon_f| \ll \Gamma$, represented by $\epsilon_f = 0$. In Fig. 1 we have plotted the impurity susceptibility, $\chi(T)$, in response to a field that couples linearly to one of the impurity moments—either the magnetic moment in the case of a magnetic field or the quadrupolar moment in the case of an electric or strain field (the two susceptibilities are identical for $\epsilon_f = 0$). In a Fermi liquid, $\chi(T)$ saturates at a constant as $T \to 0$. Here it diverges logarithmically with decreasing temperature, consistent with the NFL behavior of the two-channel Kondo model [7]. The logarithmic temperature dependence extends from weak coupling ($\Gamma/D \approx 0.03$ in Fig. 1) to strong coupling ($\Gamma/D \approx 0.8$). Thus, the same critical behavior of the integer-valent limit persists into the mixed-valent regime.

The crossover to logarithmic temperature dependence in Fig. 1 is associated with a characteristic energy scale or Kondo temperature, T_K, defined as the temperature at which the effective moment per unit occupancy, $\mu_{\text{eff}}(T) \equiv T\chi_i(T)/n_i(T)$, is 60% screened. Here $n_i(T)$ and $\chi_i(T)$ are the occupancy and susceptibility of the corresponding $5f^i$ doublet ($i = 2,3$; we use $\mu_B g_i = 1$, except in Fig. 3 below). Note that the f-electron count is given by $3 - n_2(T)$, and that $n_i(T)$ is fixed at one-half for $\epsilon_f = 0$. At high temperature, $\mu_{\text{eff}}(T)$ reduces to the free-moment value of one-quarter. Hence T_K is defined by $\mu_{\text{eff}}(T_K) = 0.1$. For the cases shown in Fig. 1, this definition gives good agreement (within 25%) with a slope of $1/20T_K$ for the logarithmic component of $\chi_i(T)/n_i(T)$, as is characteristic of the two-channel Kondo effect [13].

Figure 2 depicts the Kondo temperature T_K as a function of Γ, for $\epsilon_f = 0$. Rather than varying exponentially with $1/\Gamma$, over the range $0.01 < \Gamma/D < 0.2$ we find the power-law dependence $T_K \sim \Gamma^x$, with $x \approx 0.9$. This behavior is very close to the linear dependence expected from simple renormalization-group (and analytic NCA) arguments. However, we find $T_K/\Gamma \approx 0.2$, which is not expected from the renormalization-group and NCA arguments. For a representative value $\Gamma = 0.3$ eV, this ratio

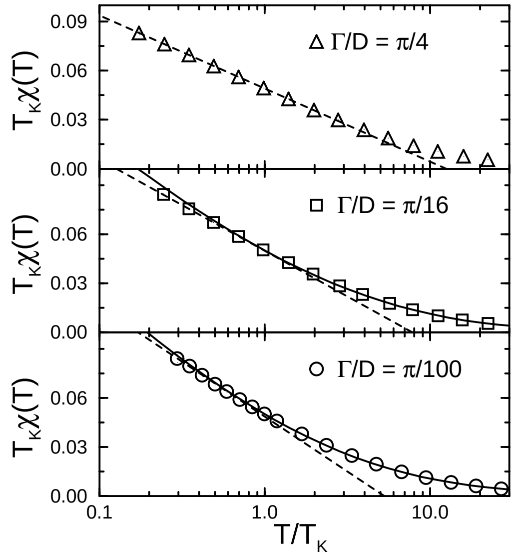

FIG. 1. The impurity susceptibility, $\chi(T)$, for $\epsilon_f = 0$ and different Γ/D. $\chi(T)$ is defined as the response to a field that couples linearly to one of the impurity moments (for $\epsilon_f = 0$, the magnetic and quadrupolar susceptibilities are identical). Error bars are smaller than the symbols used. For $T < T_K$ (T_K the Kondo scale), $\chi(T)$ has the logarithmic temperature dependence $\chi(T) \sim (a/T_K)\log(T_K/T)$, with a extracted from a logarithimic fit (dashed lines). In going from large to small Γ/D, a takes the values 0.019, 0.024, and 0.029, while T_K/D equals 0.09, 0.032, and 0.00662, respectively. The solid lines in the middle and lower graphs are the results of the NCA with $\Gamma/D = \pi/23$ and $\Gamma/D = \pi/144$, respectively (see text). There is excellent agreement between the NCA and the Monte Carlo results down to $T/T_K \approx 0.7$, at which point the NCA curves cross over to a logarithmic temperature dependence with $a = 0.037$ and 0.042 for $\Gamma/D = \pi/23$ and $\Gamma/D = \pi/144$, respectively.

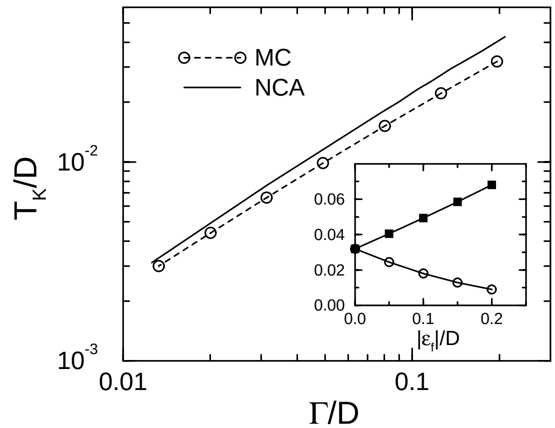

FIG. 2. T_K versus Γ, for $\epsilon_f = 0$. Open circles are the results of the Monte Carlo techniques; full line was obtained using the NCA. Error bars for the Monte Carlo data are smaller than the symbols used. Inset: The screening temperatures T_K/D (open circles) and T_{ex}/D (filled squares) as a function of $|\epsilon_f|/D$, for fixed $\Gamma/D = \pi/16$ (results obtained using Monte Carlo technique).

gives a Kondo temperature of $T_K \sim 600$ K, i.e., 60-fold larger than the 10 K seen in UBe_{13}. Hence, contrary to previous claims for an uranium ion with full spherical symmetry [14], our model does not support a small energy scale in the limit of strong valence fluctuations.

Figure 2 also presents a comparison between the Monte Carlo approach and the NCA [5]. Within the NCA, the low-energy physics is exclusively determined by the ratio of the spin degeneracy to the number of independent conduction-electron channels [5]. Thus, irrespective of the interconfigurational energy ϵ_f, the NCA yields the critical behavior of the two-channel Kondo model for the Hamiltonian of Eq. (1), in agreement with the Monte Carlo result. In Fig. 2, the NCA curve for T_K is slightly shifted (on a log-log scale) with respect to the Monte Carlo curve. This shift may be accounted for by rescaling Γ^{NCA} relative to Γ^{MC}, which we attribute in part to the different high-energy cutoff schemes used in the two formulations. By matching the NCA and the Monte Carlo occupation numbers away from $\epsilon_f = 0$, we extracted the rescaling factor $\Gamma^{MC}/\Gamma^{NCA} \approx 1.44$. Using this rescaling, one obtains good quantitative agreement between the Monte Carlo and the NCA results throughout the mixed-valent regime, as is exemplified in Fig. 1 for the scaled susceptibility, $T_K\chi(T)$.

In going to $\epsilon_f \neq 0$, the spin and the quadrupolar moments are no longer screened at the same temperature. Specifically, the moment associated with the excited doublet is quenched first at a characteristic temperature T_{ex}, followed by the moment associated with the low-lying doublet which is screened at $T_K < T_{ex}$. Physically, each screening temperature represents a different crossover. Screening of the excited doublet sets in as the occupancy of that doublet crosses over from a high-temperature free-ion (Boltzmann) form to one that is governed by valence fluctuations. On the other hand, T_K marks the crossover to strong coupling and the onset of NFL behavior.

In the inset of Fig. 2 we have plotted T_{ex} and T_K as a function of $|\epsilon_f|$, for $\Gamma/D = \pi/16$. The ground-state occupancy of the $5f^2$ doublet ranges in this plot from $n_2 = 0.29$ for $\epsilon_f = 0.2$ to $n_2 = 0.71$ for $\epsilon_f = -0.2$. Note that T_{ex} and T_K interchange meanings, depending on the sign of ϵ_f: For $\epsilon_f > 0$, T_{ex} and T_K are the screening temperatures for the quadrupolar and the magnetic moments, respectively; for $\epsilon_f < 0$, the roles are reversed.

As seen in Fig. 2, T_{ex} grows essentially linearly with $|\epsilon_f|$. This stems from the fact that the free-ion occupancy of the excited doublet decays exponentially with $|\epsilon_f|/T$. Consequently, the crossover to an occupancy driven by charge fluctuations is exponentially sensitive to $|\epsilon_f|/T_{ex}$. Contrary to T_{ex}, T_K decreases with increasing $|\epsilon_f|$, becoming exponentially small for $|\epsilon_f| \gg \Gamma$. Extracting the ratio T_K/Γ for $|\epsilon_f| = 0.2$ and using the value $\Gamma = 0.3$eV, one obtains $T_K \sim 150$ K, which is still an order of magnitude too large to explain the 10 K observed in UBe_{13}.

Finally, we have computed the nonlinear susceptibility, $\chi^{(3)}$, defined from expansion of the magnetization in the direction of the applied field: $M(H) = \chi^{(1)}H +$

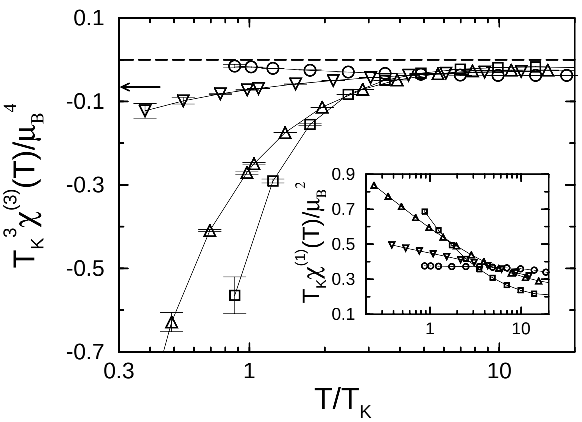

FIG. 3. $\chi^{(3)}(T)$ along the (100) direction, for $\Gamma/D = \pi/16$ and $\epsilon_f/D = -0.2$ (∘), -0.08 (▽), 0 (△), and 0.2 (□). The corresponding ground-state $5f^2$ weights equal 0.71, 0.59, 0.5, and 0.29, respectively, while $T_K/D = 0.032$, 0.02, and 0.009 for $|\epsilon_f|/D = 0$, 0.08, and 0.2. Inset: Linear susceptibility for the same set of parameters. For $T_K \approx 10$ K, as appropriate for UBe_{13}, $\chi^{(3)}(T = T_K) \approx -0.12$ emu/mole T^3 for $\epsilon_f/D = -0.08$, in close agreement with experiment [3,4] (corresponding value for UBe_{13} is indicated by the arrow). Similarly, $\chi^{(1)}(0) \approx 0.014$ emu/mole for the $\epsilon_f/D = -0.2$ case, compared with an experimental value of 0.012–0.016 emu/mole.

$\frac{1}{3!}\chi^{(3)}H^3 + \ldots$. For UBe_{13}, in addition to linear splitting of the $5f^3$ magnetic doublet, a finite magnetic field induces a van Vleck splitting and an overall shift of the $5f^2$ quadrupolar doublet, due to matrix elements between the Γ_3 ground doublet and excited CEF multiplets. We have included this effect by computing the Γ_3 energy shifts perturbatively, up to fourth order in H. The first excited CEF levels at $\Delta_{\mathrm{CEF}} \approx 15$ meV [15] were assumed to be degenerate Γ_4 and Γ_5 triplets, chosen to allow the van Vleck contribution to the linear susceptibility to quantitatively match the UBe_{13} data, as discussed in Ref. [2]. This also fixed the position of the Γ_1 level. To make contact with experiment, we fixed the ratio $T_K/\Delta_{\mathrm{CEF}} \approx 0.055$, which is necessary to account for the overestimated Kondo temperatures in our calculations.

The resulting $\chi^{(3)}(T)$ curves are shown in Fig. 3. From these calculations it is apparent that only for $\epsilon_f/D \approx -0.08$, which corresponds to a ground-state f^2 occupancy of about 60%, can one obtain a curve quantitatively compatible with the pure UBe_{13} data. The curve for $\epsilon_f/D = -0.2$ (about 70% ground-state f^2 weight) resembles that for $U_{0.9}Th_{0.1}Be_{13}$. In contrast, the $\epsilon_f/D = 0$ and 0.2 curves have too strong a temperature dependence to correspond with experiment, both for the nonlinear *and* linear susceptibility (inset to Fig. 3). In every case, the characteristic energy scale is too large for all of these mixed-valent runs to account for the experimental data. We conclude that the scenario of Aliev *et al.* [4], suggesting that UBe_{13} is a more strongly mixed valent than anticipated previously, and that doping with Th increases the $5f^2$ weight (driving the system closer to the quadrupolar Kondo limit), is qualitatively consistent with our results.

The most severe omission from our model is a proper *dynamical* treatment of excited CEF triplets (beyond perturbative shifting of the bare Γ_3 levels). Although these triplets possess negligible Boltzmann weights in the ionic limit, they can have significant zero-temperature quantum weights for nonzero hybridization. Because of their magnetic character, their inclusion can potentially render the $\chi^{(3)}$ curves more negative even in the $5f^2$ limit. They also introduce (even in the mixed-valent limit) a small energy scale associated with crossover physics between ground-state screening of the Γ_3 doublet and collective screening of the entire Hund's rule multiplet [16].

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[16] See Sec. 5.3.2 of Ref. [3]. The possibility of such a small crossover scale has been recently confirmed by M. Koga, by explicit numerical renormalization-group calculations.