Small Energy Scale for Mixed-Valent Uranium Materials

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We investigate a two-channel Anderson impurity model with a $5f^1$ magnetic and a $5f^2$ quadrupolar ground doublet and a $5f^2$ excited triplet. Using the numerical renormalization group method, we find a crossover to a non-Fermi-liquid state below a temperature T^* varying as the $5f^2$ triplet-doublet splitting to the $7/2$ power. To within numerical accuracy, the nonlinear magnetic susceptibility and the $5f^1$ contribution to the linear susceptibility are given by universal one-parameter scaling functions. These results may explain UBe_{13} as mixed valent with a small crossover scale T^*. [S0031-9007(99)08723-2]

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The possibility of non-Fermi-liquid (NFL) behavior in Ce- and U-based alloys has been discussed intensively since the discovery of the anomalous temperature dependence of their resistivity, magnetic susceptibility, and specific heat coefficient. A candidate for the explanation of the NFL state is the multichannel Kondo model, widely used for the f-shell materials [1]. For the f-shell impurities, the intra-atomic interactions such as Hund's and spin-orbit couplings have to be taken into account in the presence of the crystalline electric field (CEF), giving rise to various types of scattering of conduction electrons [2,3]. Experimental investigations of dilute Ce or U alloys suggested that single-site effects of such a magnetic ion are important for NFL physics. In the U case, the observation of a logarithmically divergent specific heat coefficient [4] strongly supported the quadrupolar (two-channel) Kondo scenario [5]. As evidence of single-site U effects, such a logarithmic anomaly was observed in the dilute U limit of $U_xTh_{1-x}Ru_2Si_2$ [6], although the resistivity in this metal cannot be explained by the simple two-channel Kondo model [7].

According to photoemission and inverse photoemission studies on U compounds [8], well-separated atomiclike peaks cannot be seen in $5f$ spectra, while for Ce compounds the peaks can be described by an Anderson impurity model. This implies that $5f$ properties look much more like mixed valence. Recently, the two-channel Anderson impurity model in the mixed-valent regime was proposed to account for the NFL physics of UBe_{13} [9]. In this model, a low-lying Γ_3 quadrupolar (non-Kramers) doublet in the $5f^2$ configuration and a Γ_6 magnetic (Kramers) doublet in the $5f^3$ configuration are taken into account and excited CEF states are neglected. Both states mix with each other via the hybridization between the localized f orbital and conduction band. The model successfully describes the temperature dependence of the nonlinear magnetic susceptibility observed in UBe_{13} [10] and in $U_{1-x}Th_xBe_{13}$ [11], suggesting that strong quantum fluctuations should drive the CEF state of U ions to a mixed-valent state between U^{+3} and U^{+4} [11]. However, except for virtual effects like the Van Vleck magnetic susceptibility, excited $5f^2$ CEF levels were neglected in the model. This leaves a large question, however: how can the small energy scale ($\simeq$10 K) apparent in thermodynamic data for, e.g., UBe_{13} be reconciled with such a mixed-valence model for which the smallest plausible value is large ($\simeq$150 K)?

In this paper, we show that the inclusion of the excited CEF levels resolves all the above controversies. The dynamics of the excited CEF states reduces the crossover temperature to the two-channel Kondo state significantly even in the mixed-valent regime. Using Wilson's numerical renormalization group (NRG) method [12,13] for a cubic CEF case, we show clearly that a small energy scale T^* is related to the competition between different types of NFL fixed points, which is very important for explaining the observed nonlinear susceptibility within the two-channel Kondo scenario. The crossover in the Kondo effect is visualized by flows of NRG energy levels, and T^* can be estimated by observing the recovery of the symmetry associated with the two-channel Kondo model. We find that T^* obeys a power law with respect to the CEF splitting and can be much smaller as the splitting decreases. In addition, the nonlinear magnetic susceptibility is dominated by the magnetic moment of the excited configuration and obeys a one-parameter scaling law set by T^*. We expect this result for the small energy scale to be generic for ions such as Pr, Tm, and U which fluctuate between configurations with internal degrees of freedom; the exponent of the power law will vary with the details of the CEF spectrum of the ground configuration.

In the present work, we study the two-channel Anderson impurity model in a cubic system, taking into account the first excited Γ_4 triplet state explicitly as well as the lowest-lying Γ_3 quadrupolar doublet in $5f^2$: both states are coupled to the Γ_7 magnetic doublet (the lowest possible state in $5f^1$) via the hybridization V with the Γ_8 conduction electrons. Note that the choice of $5f^1$ in our work is motivated by calculational simplicity; there is no qualitative difference with respect to the $5f^2$-$5f^3$ picture used in Ref. [9]. The corresponding Hamiltonian is given by

$$H = \sum_{km} \varepsilon_k c_{km}^\dagger c_{km} + \sum_M E_M |M\rangle\langle M| + V \sum_{km\alpha M} (C_{\alpha,m;M} c_{km}^\dagger |\alpha\rangle\langle M| + \text{H.c.}), \quad (1)$$

where a single-f-electron state $|\alpha\rangle$ represents the Γ_7 states and a two-f-electron state $|M\rangle$ represents the Γ_3 and Γ_4 states. The operator $c_{km}^\dagger$ (c_{km}) creates (annihilates) a Γ_8 conduction electron with a wave number k, the kinetic energy of which is given by ε_k. The energy of the f-electron state E_M ($= E_{\Gamma_3}, E_{\Gamma_4}$) is measured from that of the Γ_7 magnetic doublet. The Clebsch-Gordan coefficient $C_{\alpha,m;M}$ is given by $\langle\alpha|f_m|M\rangle$, where f_m annihilates an f electron with Γ_8 symmetry. If the energy of the Γ_4 triplet state is so large that the contribution from the triplet can be neglected, the Hamiltonian (1) becomes simpler as presented in Ref. [9]. Assuming further that $\pi\rho V^2 \ll |E_{\Gamma_3}|$ (ρ is the conduction-electron density of states at the Fermi level), the Hamiltonian is reduced to the two-channel Kondo Hamiltonian with $S = 1/2$ (S is the size of a local spin) [2,5], which has been solved by various methods [1]. We can label the four Γ_8 states by a tensor product of two quadrupolar and two magnetic indices. Each of them has SU(2) symmetry in the restricted Hilbert space of this isotropic Hamiltonian. In our model, on the other hand, we have to treat the cubic symmetry explicitly because mixing of Γ_3 and Γ_4 states prevents the SU(2) labels from being good quantum numbers.

In spite of such a complicated atomic structure of the impurity, the Hamiltonian (1) can be solved by the NRG method [12,13]. For the purpose of numerical calculation, it is transformed to the following hopping Hamiltonian with the recursion relation

$$H_{N+1} = \Lambda^{1/2} H_N + \sum_m (s_{N+1,m}^\dagger s_{Nm} + \text{H.c.}),$$
$$H_0 = \Lambda^{-1/2} \left[\sum_M \tilde{E}_M |M\rangle\langle M| + \tilde{\Gamma}^{1/2} \sum_{m\alpha M} (C_{\alpha,m;M} s_{0m}^\dagger |\alpha\rangle\langle M| + \text{H.c.}) \right]. \quad (2)$$

Here H_0 describes the impurity site, and $s_{nm}^\dagger$ creates a Γ_8 electron in the conduction band discretized logarithmically as D/Λ (D is a half-width of the band). The energy of two f-electron states $\tilde{E}_M$ and the hybridization $\tilde{\Gamma}$ are equal to E_M/D and $\rho V^2/D$, respectively, except for some Λ-dependent scaling factors [13]. We diagonalize the NRG Hamiltonian H_N at each NRG step to solve the eigenenergies, and we construct H_{N+1} from H_N, using the Clebsch-Gordan method for the cubic symmetry [14], which speeds up the calculation tenfold. Introducing an axial magnetic field $h_{z,0}$ on the impurity site, we can calculate the temperature T dependence of the impurity magnetization by using

$$M_z = \frac{\text{Tr}\, J_z \exp[-\bar{\beta}(H_N + H_N')]}{\text{Tr} \exp[-\bar{\beta}(H_N + H_N')]}. \quad (3)$$

Here the axial component J_z of the total angular momentum is coupled to the magnetic field in the Zeeman term $H_N' = -g_J J_z h_z$ (g_J is a Landé's g factor and we take $\mu_B = k_B = 1$). The physical temperature T and the rescaled magnetic field h_z are given by

$$T = \frac{1 + \Lambda^{-1}}{2} \Lambda^{-(N-1)/2}/\bar{\beta},$$
$$h_z = \frac{2}{1 + \Lambda^{-1}} \Lambda^{(N-1)/2} h_{z,0}, \quad (4)$$

respectively, where we take $\bar{\beta} \sim 2$. The linear susceptibility $\chi_{\text{imp}}^{(1)}$ and nonlinear susceptibility $\chi_{\text{imp}}^{(3)}$ are calculated by expanding M_z in $h_{z,0}$ ($M = \chi^{(1)} h + \chi^{(3)} h^3/6 + \ldots$). In the NRG calculation, these are explicitly given by

$$T\chi_{\text{imp}}^{(1)} = \bar{\beta}^{-1} \lim_{h_z \to 0} [M_z(h_z) - M(0)]/h_z,$$
$$T^3 \chi_{\text{imp}}^{(3)} = 6\bar{\beta}^{-3} \lim_{h_z \to 0} [M_z(h_z) - \bar{\beta} T \chi_{\text{imp}}^{(1)} h_z]/h_z^3. \quad (5)$$

This calculation of the impurity susceptibility gives sufficient accuracy over a wide range of temperatures, as long as the hybridization V is restricted to $\pi\rho V^2 \ll D$. Throughout the NRG calculations, we take $\Lambda = 3$ and keep 500 or 800 lowest-lying states at each NRG step. Although the latter number reduces the numerical error relative to the former, a qualitative difference does not appear. We show the former results in this paper.

First, we briefly discuss the case $E_{\Gamma_4} \gg E_{\Gamma_3}$ in the mixed-valent regime [9]. As the temperature decreases, two characteristic temperatures are obtained: at a higher temperature, the highest of the Γ_3 quadrupolar and Γ_7 magnetic doublets is screened by the conduction electrons; at a lower temperature, the other doublet is screened. The NFL behavior due to the two-channel Kondo effect appears at the lower temperature T_K. T_K increases with the increase of V and the decrease of $|E_{\Gamma_3}|$. According to the analysis for the realistic parameter region of the Hamiltonian, the evaluated T_K is larger by an order of magnitude than the 10 K observed in UBe_{13}. If the contribution from the Γ_4 triplet to the Kondo effect is taken into account, T_K is enhanced as the CEF splitting $\Delta = E_{\Gamma_4} - E_{\Gamma_3} (>0)$ approaches zero, and a smaller temperature T^* appears at which we find the crossover from the CEF states to the NFL states. Below we discuss this energy scale, restricting ourselves to the realistic case where f^2 is the most stable configuration ($E_{\Gamma_3} < E_{\Gamma_4} < 0$) and the two-channel Kondo effect occurs at low temperatures.

Our NRG results show that the stable fixed points are classified into two types: for the first, the low-lying excitations can be described by assuming a Γ_3 local moment coupled to the conduction electrons. For the second, a Γ_4 local moment is dominant in the low-lying excitations. The stability of the fixed points depends on whether the bare CEF splitting Δ is above or below a critical value Δ_c (>0). The following discussion is restricted to the case $\Delta' = \Delta - \Delta_c > 0$ where we obtain the first fixed point, described by the two-channel Kondo model, as is easily found from a flow diagram of the low-lying NRG energy levels in Fig. 1. For a small number of NRG steps, the almost degenerate $(0, \Gamma_3)$ and $(0, \Gamma_4)$ states correspond to the lowest-lying CEF states with small splitting Δ. As the number of NRG steps increases, the splitting of $(0, \Gamma_3)$ and $(0, \Gamma_4)$ levels becomes larger and the former becomes the lowest state at the fixed point (where all the NRG energy levels reach constant values). The double degeneracy of Γ_3 corresponds to that of a local spin of the two-channel Kondo model [5]. Practically, we define T^* as the temperature corresponding to the number of NRG steps at which the difference of the NRG energy levels between the $(0, \Gamma_4)$ and $(0, \Gamma_5)$ triplets reduces to 0.01. The degeneracy of these states is one piece of evidence for the two-channel Kondo fixed point.

Figure 2 shows that T^* is proportional to the power law with an effective CEF splitting Δ^*. In analogy with Boltzmann weight factors, Δ^* is associated with the occupancy weights of f electrons n_3^* and n_4^* in the Γ_3 doublet and Γ_4 triplet at the fixed point, respectively:

$$\Delta^* = \Delta_0 \ln\left(\frac{3n_3^*}{2n_4^*}\right). \tag{6}$$

Here Δ_0 depends on only the hybridization $\tilde{\Gamma}$ if the other parameters are fixed. When Δ^* goes to zero with Δ', both the Γ_3 doublet and Γ_4 triplet become relevant with the same weight. Each line in Fig. 2 has almost the same power, implying $T^* \propto (\Delta^*)^{7/2}$. As Δ' approaches zero (we use the NRG scale $\tilde{\Delta}' = 2/[1 + \Lambda^{-1}]\Delta'$ in Fig. 2), it tends to be proportional to Δ^* and satisfies $T^* \propto (\Delta')^{7/2}$. This relation can be derived from the equation for a small energy scale $T_{\mathrm{CEF}}^{\mathrm{x}} \simeq T_0(\Delta/T_0)^2/4$ appearing in Sec. 5.3.2 of Ref. [1]. Since T_0 is the temperature at which the Γ_3 doublet is screened by the conduction electrons, written as $T_0 = (D/\Delta)^{3/2} T_{\mathrm{K},\Gamma_3}$, where T_{K,Γ_3} is the Kondo temperature for the case without the higher Γ_4 triplet [15], we obtain

$$T_{\mathrm{CEF}}^{\mathrm{x}} \simeq \frac{1}{4} \frac{D^2}{T_{\mathrm{K},\Gamma_3}} \left(\frac{\Delta}{D}\right)^{7/2}. \tag{7}$$

This resembles the relation of T^* and Δ' if Δ' is small. Actually the hybridization renormalizes Δ to Δ' as obtained by our NRG calculation. For the two-channel Kondo effect, T_{K,Γ_3} is given by $\rho V_{\mathrm{eff}}^2 \exp(E_{\Gamma_3}/2\rho V_{\mathrm{eff}}^2)$, where the ratio $V_{\mathrm{eff}}^2/V^2 = 8/21$ comes from a Clebsch-Gordan coefficient when we derive the effective exchange interaction due to the Γ_3 doublet. Using Eq. (7), we can roughly estimate the ratio $T^*/(\Delta')^{7/2}$ as $1/(10^6 T_{\mathrm{K},\Gamma_3})$, where D is taken to be unity.

In Fig. 3, we show the temperature dependent magnetic susceptibility rescaled by T^*. The linear susceptibility $\chi_{\mathrm{imp}}^{(1)}$ is approximately given as a sum of Zeeman and Van Vleck parts. The former term is dominated by the Γ_7 magnetic susceptibility $\chi_{\mathrm{imp},\Gamma_7}^{(1)}$. Each curve $\chi_{\mathrm{imp},\Gamma_7}^{(1)}$ is well fitted by a function $f(T/T_s)/T_s$, logarithmic below $T \simeq T_s$ ($T_s \simeq 10T^*$). On the contrary, such a simple scaling function cannot be found for the Van Vleck contribution, which is expected to be given by $a - b\sqrt{T/T_s}$

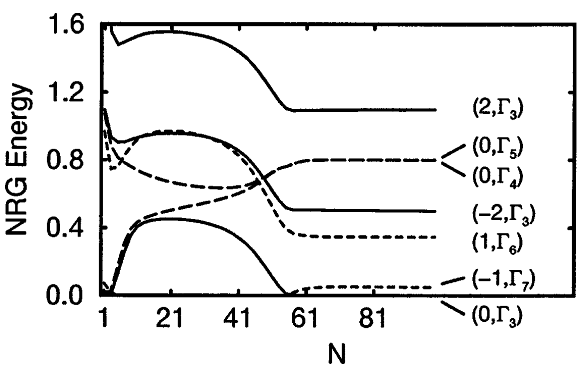

FIG. 1. Flow of the most relevant NRG energy levels for the odd number of NRG steps N and $\Lambda = 3$. We take $\tilde{\Gamma} = 0.15$, $\tilde{E}_{\Gamma_3} = -0.200$, and $\tilde{E}_{\Gamma_4} = -0.168$ here. Each energy level is labeled by (Q, Γ_i), where Q represents the total number of particles measured with respect to the ground state. At the fixed point, the $(-1, \Gamma_7)$ and $(1, \Gamma_6)$ doublets have a center of gravity energy of 0.2, while the degenerate $(0, \Gamma_4)$ and $(0, \Gamma_5)$ triplets have an energy of 0.8. These values correspond to the first and second excited NRG energies given by the two-channel Kondo model for $\Lambda = 3$ [18]. This implies that only particle-hole symmetry breaking causes the splitting of the $(-1, \Gamma_7)$ and $(1, \Gamma_6)$ doublets and that of the $(-2, \Gamma_3)$ and $(2, \Gamma_3)$ doublets.

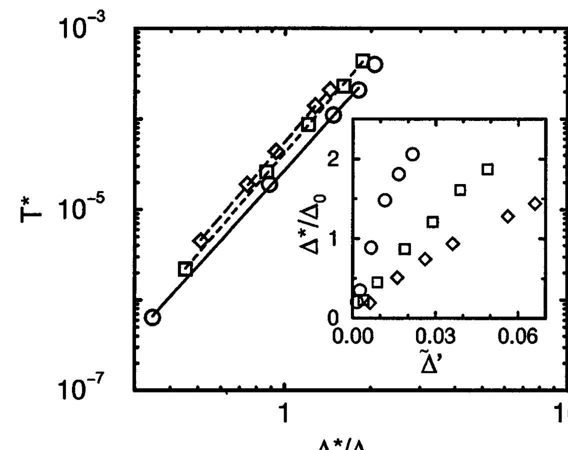

FIG. 2. Relation between the small energy scale T^* and the effective CEF splitting Δ^* for $\tilde{\Gamma} = 0.10$ (∘), 0.15 (□), and 0.20 (◇), where we fix $\tilde{E}_{\Gamma_3}$ at -0.200. The corresponding lines are represented by $T^* = a(\Delta^*/\Delta_0)^b$, given as $(a, b) = (2.7 \times 10^{-5}, 3.5)$, $(4.2 \times 10^{-5}, 3.7)$, and $(5.6 \times 10^{-5}, 3.7)$, respectively. Inset: Δ^*/Δ_0 versus $\tilde{\Delta}'$ ($= 3[\Delta - \Delta_c]/2$). For the above ordering of $\tilde{\Gamma}$ values, $3\Delta_c/2$ is 0.018, 0.031, and 0.044.

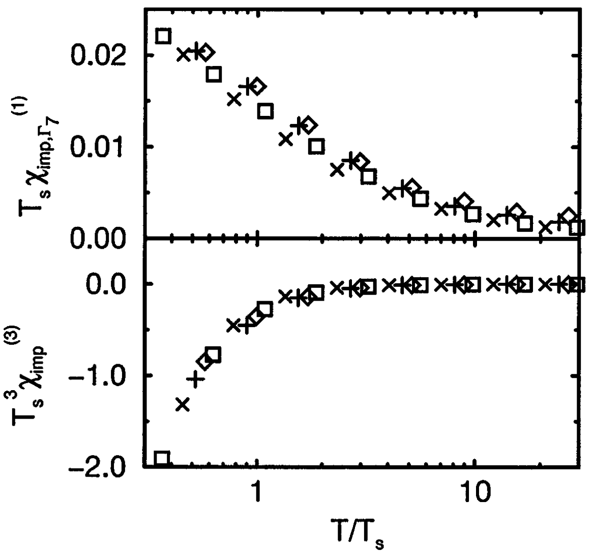

FIG. 3. Temperature dependent impurity magnetic susceptibility. The curves are for $\tilde{\Gamma} = 0.10$, $\tilde{E}_{\Gamma_3} = -0.200$, and $\tilde{E}_{\Gamma_4} = -0.160$ ($\diamond$), -0.165 ($+$), -0.170 ($\square$), and -0.175 ($\times$); for which, T_s ($\simeq 10T^*$) is, respectively, 3.6×10^{-3}, 2.3×10^{-3}, 1.1×10^{-3}, and 1.7×10^{-4}, and the $5f^2$ occupancy in the ground state is 0.775, 0.765, 0.751, and 0.727, respectively. Upper curve: The $5f^1$ contribution to the linear susceptibility $\chi^{(1)}_{\rm imp}$. Lower curve: The total nonlinear susceptibility.

[16]. In this case, a and b appear to be complicated functions of T^* and Δ^*. Since $|\langle\Gamma_3|J_z|\Gamma_4\rangle|^2/\Delta$ is very large in our model, mainly the Van Vleck part contributes to $\chi^{(1)}_{\rm imp}$ and, thus, a simple scaling relation for $\chi^{(1)}_{\rm imp}$ cannot be found.

On the other hand, the curves for the nonlinear susceptibility $T_s^3\chi^{(3)}_{\rm imp}$ do scale with T/T_s, implying that the main contribution comes from the Γ_7 magnetic doublet even when f^2 is more stable than f^1 ($0.5 < n_3^* + n_4^* \lesssim 0.8$). Usually the Γ_3 quadrupolar moment gives rise to a positive $\log(T_{K,\Gamma_3}/T)$ dependence in $\chi^{(3)}_{\rm imp}$ due to the two-channel Kondo effect, which should be caused by the Van Vleck coupling of the Γ_3 doublet and Γ_4 triplet. However, the magnetic part derived from the Γ_7 behaves as $-1/T^3 \rightarrow -1/T$ below T_s and overcomes the quadrupolar contribution. This trend of negative $\chi^{(3)}_{\rm imp}$ is in good agreement with the nonlinear susceptibility derived by the simple model where the dynamics of the Γ_4 triplet was neglected [9]. However, for comparison of the scaling behavior, T_K must be replaced by T_s. For $E_{\Gamma_3} < 0$, T_K is approximately equal to T_{K,Γ_3} in Eq. (7) and is very large in the strongly mixed-valent regime. On the other hand, T^* ($\simeq 0.1T_s$) can be much smaller when Δ is close to Δ_c. We conclude that T^*, characteristic to the competition between the two different types of NFL fixed points, can represent the small energy scale of around 10 K for UBe_{13}.

As discussed above, the low-energy physics below T^* is described very well by the two-channel Kondo model as long as the CEF splitting satisfies $\Delta > \Delta_c$. In the case $\Delta < \Delta_c$, low-lying excitations dominated by the relevant triplet at low temperatures are very different from those given by the two-channel Kondo model. The study of this case is also required and motivated by a recent experiment of $U_xY_{1-x}Pd_3$ where a Γ_5 triplet is almost degenerate with a Γ_3 doublet [17]. We anticipate that a small crossover scale will still result for $\Delta < \Delta_c$, albeit with a different power law exponent. Indeed, this result should be generic for mixed-valent ions, such as Pr and Tm, having configurations with internal degrees of freedom for the lowest CEF levels.

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