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Role of the d-f Coulomb interaction in intermediate valence and Kondo systems: a numerical renormalization group study

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Abstract. Using the numerical renormalization group method, the dependences on temperature of the magnetic susceptibility $\chi(T)$ and specific heat $C(T)$ are obtained for the single-impurity Anderson model with inclusion of d-f the Coulomb interaction. It is shown that the exciton effects caused by this effect (charge fluctuations) can significantly change the behaviour of $C(T)$ in comparison with the standard Anderson model at moderately low temperatures, whereas the behaviour of $\chi(T)$ remains nearly universal. The ground-state and temperature-dependent renormalizations of the effective hybridization parameter and f-level position caused by the d-f interaction are calculated, and satisfactory agreement with the Hartree-Fock approximation is derived.

PACS. 71.27.+a Strongly correlated electron systems; heavy fermions – 71.28.+d Narrow-band systems; intermediate-valence solids – 75.30.Mb Valence fluctuation, Kondo lattice, and heavy-fermion phenomena

1 Introduction

The $4f$-electron compounds represent an interesting system demonstrating intermediate valence (IV) of rare earth elements (usually between 2+ and 3+) in a number of properties. For example, this includes among several things, the lattice parameters (which are intermediate between those for isostructural compounds with di- and trivalent ions), and core-level spectra (which are mixtures of the spectra for di- and trivalent ions with comparable weights). Heavy fermion (HF) compounds form another important class of f-electron systems with anomalous properties [5]. For the HF metals, it is commonly accepted now that they are Kondo lattices, meaning that their small energy scale electron properties are described in terms of the Kondo temperature $T_{\rm K}$, i.e. the width of the Kondo resonance due to spin-dependent scattering of conduction electrons by f-electron centres [6]. Intermediate valence compounds are also frequently considered to possess Kondo lattices, but with higher $T_{\rm K}$ (e.g. see reference [4]).

However, this description is not strictly correct since, in addition to spin ("Kondo") fluctuations, valence or *charge* fluctuations should also be included in models of these systems. They are determined in part by the Coulomb repulsion G between conduction and localized electrons (the Falicov-Kimball interaction [7]). Taking into account the d-f interaction, together with the hybridization processes, it is possible to describe the IV state as being a kind of exciton condensation [8,9]. Recently, first-principles calculations of the parameter G have been proposed. These demonstrate that proper account of this interaction is necessary to describe the equation of state for the IV phase of Yb under pressure [10].

At present, the normal Kondo effect is rigorously described by the s-d exchange (Kondo) and Anderson models. Moreover, for one-impurity situations, the exact numerical (renormalization group) [11,12] and analytical Bethe-ansatz [13,14] solutions to this problem are known. Universal curves exist that describe the behaviour of thermodynamic properties for the Kondo [11,12] and intermediate valence [12] regimes. These permit a detailed comparison with experimental data for anomalous f-systems. However, similarly detailed information is not available in the presence of both the s-d exchange and Coulomb interaction.

Formally, the charge fluctuations can be also described in terms of a pseudo-Kondo effect: the states with (without) an f-hole are considered as pseudospin-up (down) states (respectively) [15,16]. It is the degeneracy of quantum states for a scattering centre that is crucial for the formation of the Kondo resonance [17]. In the IV case, the divalent and trivalent states are degenerate by definition; thus, this analogy is not surprising. Therefore, it is natural to consider the Kondo phenomenon for the IV compounds taking into account both spin and charge fluctuations;

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or, equivalently, both the "Kondo" and exciton ("Falicov-Kimball") effects. According to reference [12], the additional d-f Coulomb interaction is a marginal operator of the valence fluctuation fixed point.

Since there is no clear demarcation between the IV and Kondo systems, it can be supposed that the exciton effects are also relevant for the latter case. Recent analysis of the interplay between true Kondo and pseudo-Kondo (exciton) effects [18] by the "poor-man's scaling" approach [19,20], demonstrates that there is a crucial modification of the low-energy (infrared) behaviour, compared with pure cases of the Anderson model and Falicov-Kimball ("resonant level") models. However, this approach can give only a qualitative insight into the properties of the system. Here, we investigate the effects of this interplay by applying the numerical renormalization group (NRG) formalism [11,12].

2 Formulation of the model and computational procedure

The Hamiltonian for the asymmetric Anderson model, with inclusion of the Falicov-Kimball interaction (on-site d-f Coulomb repulsion G), is

$$\mathcal{H} = \sum_{\sigma} E_f f_\sigma^\dagger f_\sigma \ + \sum_{\mathbf{k}\sigma} \left[t_{\mathbf{k}} c_{\mathbf{k}\sigma}^\dagger c_{\mathbf{k}\sigma} + V \left(c_{\mathbf{k}\sigma}^\dagger f_\sigma + f_\sigma^\dagger c_{\mathbf{k}\sigma} \right) \right] + G \sum_{\sigma\sigma'} f_\sigma^\dagger f_\sigma c_{\sigma'}^\dagger c_{\sigma'} \quad (1)$$

where the on-site f-f Coulomb interaction U is set to infinity, so that the doubly occupied states are forbidden; and $f_{i\sigma}^\dagger = |i\sigma\rangle\langle i0|$ is the Hubbard operator ($|i\sigma\rangle$ and $|i0\rangle$ are single-occupied and empty site states). For simplicity, the dependence on $\mathbf{k}$ of the hybridization matrix element V is neglected. Physically, the choice $U = \infty$ means that interactions between *two* electron configurations only are included, i.e. f^{n-1} and f^n, but the "upper Hubbard band" associated with f^{n+1} configurations is ignored. This approximation applies well to real rare-earth compounds when the valence fluctuations involve only valences 2+ and 3+ (for Eu, Sm, Tm, and Yb) or 3+ and 4+ for Ce [1–3].

It is known that the d-f Coulomb interaction does not change the low-energy fixed point (and consequently the low-temperature behaviour): it remains the Fermi liquid fixed point of the standard impurity Anderson model (see [21]). To investigate a wider temperature interval, the standard NRG method developed earlier for the Anderson model [12] is employed, together with some important modifications. Earlier work used the NRG method to investigate the effects of Falicov-Kimball interactions: see references [22,23]. The conclusion from those calculations — that the Falicov-Kimball interaction results only in a parameter renormalization compared with the pure Anderson model — in general, is not completely accurate. It does not consider the intermediate valence regime. Furthermore, the heat capacity is not calculated; yet, as will be shown later, the deviations from the renormalized Anderson model are much more important than those in the magnetic susceptibility. The effects of the d-f interaction in the extended Anderson model on the static properties and dynamical excitation spectra — especially in the low-energy region — and on T_{K} have been investigated previously by the NRG method in reference [24].

The standard numerical renormalization group method adopts a heuristic approach to choose the optimum temperature for each NRG step [12]. An automatic procedure is introduced into the standard formalism in this work.

A finite-resolution spectrum is obtained at each NRG step. This is truncated due to the neglect of high-energy states [11]. After the Nth step of the NRG procedure a finite set of the lowest energy levels $\{E_n\}$ remains, the numerous upper energy levels being discarded at previous steps. Then, for each NRG step, an optimum temperature T_N is chosen that achieves the most exact calculation of thermodynamic averages using the subset of remaining energy levels. Indeed, the averages cannot be calculated using temperatures that are too low, otherwise the discrete nature of the energy levels causes instability in the algorithm. However, at sufficiently high temperatures the neglected high-energy states can give an appreciable contribution to the partition function. This contribution $\{E_{up}\}$ is estimated as follows. Assume that on going from $(N-1)$th to Nth iteration step, the energy of the states do not change, but their number increases by the factor of 4. Then, the average energies calculated for the Nth set of data with and without the discarded states can be compared. The average energy of the retained states is

$$\langle E \rangle_N = \frac{\sum_n E_n \exp\left(-\beta E_n\right)}{\sum_n \exp\left(-\beta E_n\right)}, \quad (2)$$

where $\beta = 1/k_{\mathrm{B}}T$). The average energy taking into account all the states is

$$\langle E \rangle_N^{\mathrm{corr}} = \frac{\sum_n E_n \exp\left(-\beta E_n\right) + \sum_{up} E_{up} \exp\left(-\beta E_{up}\right)}{\sum_n \exp\left(-\beta E_n\right) + \sum_{up} \exp\left(-\beta E_{up}\right)}. \quad (3)$$

Evidently, the difference $\langle E \rangle_N^{\mathrm{corr}} - \langle E \rangle_N$ is negligible at low temperatures, but increases with increasing T. The temperature T_N at which this difference reaches a chosen threshold ($3{\times}10^{-5} k_{\mathrm{B}}T$) is taken to be the optimum for the step N. Following this, the thermodynamic quantities can be calculated, in particular the magnetic susceptibility χ, at T_N for all steps N. At low temperatures, the material deviates from Curie's law: there is a linear decrease with temperature of the quantity $k_{\mathrm{B}}T\chi(T)/(g\mu_{\mathrm{B}})^2$, in agreement with previous results [12].

The impurity specific heat is obtained by cubic spline interpolation of the difference between total average energy and the energy of a corresponding free electron gas between different T_N, and subsequently differentiating this function with respect to T.

When performing the calculations, about 2500 states are retained, and the parameter for the logarithmic discretization of the conduction band is $\Lambda = 2$. The calculations are repeated using $\Lambda = 1.5$ to test their accuracy. These results are described in the next section.

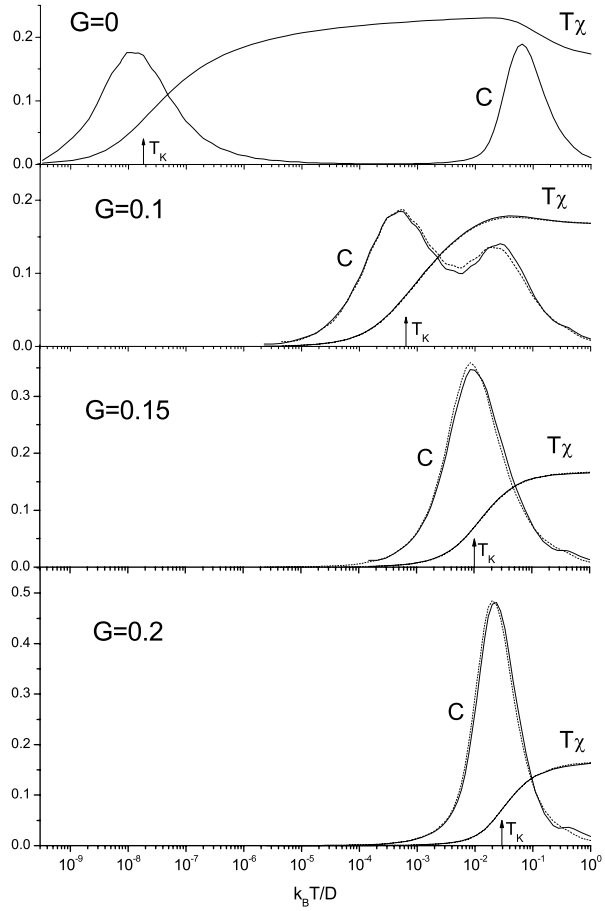

Fig. 1. The quantity $k_{\rm B}T\chi(T)/(g\mu_{\rm B})^2$ and the specific heat $C(T)/k_{\rm B}$ for $E_f = -0.14, V = 0.1$. The solid line corresponds to finite G, and the dotted line to when $G = 0$, with parameters $E_f^{(G=0)}$ and $V^{(G=0)}$ (for details see Tab. 1). Below $T_{\rm K}$ the universal Wilson curve appears.

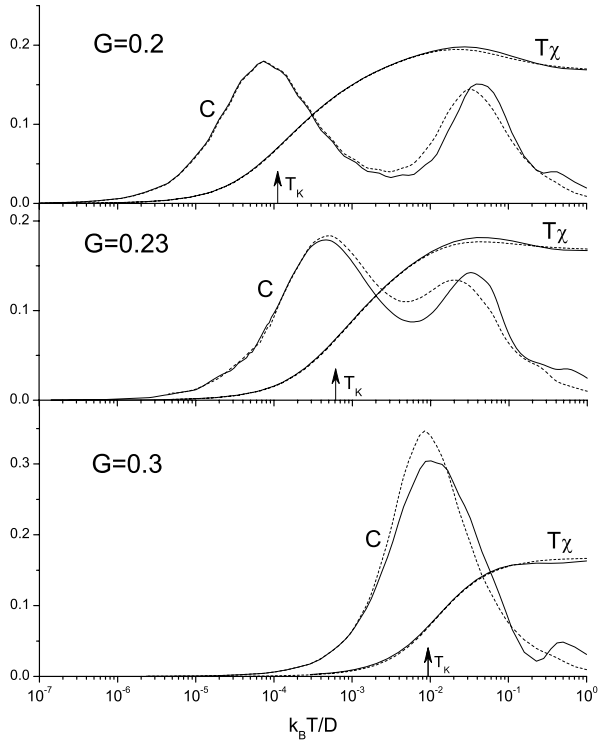

Fig. 2. The same data as in Figure 1 for $E_f = -0.25$, $V = 0.1$.

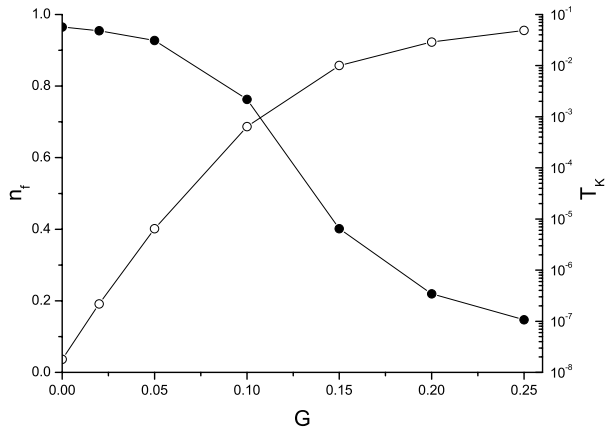

Fig. 3. The dependences on G of n_f (•) and $T_{\rm K}$ (○). ($E_f = -0.14$, $V = 0.1$).

3 Results and discussion

The results of the calculation are shown in the figures. A rectangular conduction electron density of states is used where the half-bandwidth is $D = 1$. In addition to the magnetic susceptibility and specific heat, the impurity level occupation number n_f (valence) is also calculated.

Figures 1 and 2 demonstrate a crossover from a double peak to single maximum temperature behaviour for the specific heat. It should be noted that such a crossover takes also place in the standard Anderson model with changing E_f [25]. The two peaks are well separated when $n_f \approx 1$. When n_f is small only one peak exists: the influence of the Falicov-Kimball interaction is weak, as expected from the form of the Hamiltonian. This influence is strongest in the intermediate valence case when $n_f \approx 0.7$.

One can see that the temperature dependence of the magnetic susceptibility is always similar to that for the Anderson model without the d-f Coulomb interaction. Nevertheless, the specific heat behaviour can be significantly different, especially when G is sufficiently large.

Similar to reference [12], the Kondo temperature $T_{\rm K}$ is the temperature at which $k_{\rm B}T\chi(T)/(g\mu_{\rm B})^2 = 0.0701$. The dependence on G of the ground-state f-level occupation number n_f and $T_{\rm K}$ are illustrated by Figure 3. More detailed information is presented in Table 1.

There is an important question as to whether the effects of the d-f Coulomb interaction can be described by the renormalization of the parameters usual Anderson Hamiltonian only (without the Falicov interaction), or they can result in qualitatively new effects. To investigate this problem the effective hybridization parameter $V^{(G=0)}$ and the effective position of the f-level $E_f^{(G=0)}$, are defined as as the parameters of the standard Anderson

Table 1. The dependences on G of the Kondo temperature $T_{\rm K}$ and impurity occupation number n_f for $V = 0.1$; the Hartree-Fock values $V^{\rm HF}$ and $E^{\rm HF}$ are defined by equation (4). The quantities $E_f^{(G=0)}$ and $V^{(G=0)}$ are described in the text.

E_f	G	$k_{\rm B}T_{\rm K}$	n_f	$E_f^{(G=0)}$	$E_f^{\rm HF}$	$V^{(G=0)}$	$V^{\rm HF}$
−0.06	0	7.43×10^{-5}	0.875	−0.06	−0.06	0.1	0.1
−0.06	0.01	2.23×10^{-4}	0.825	−0.049	−0.050	0.1	0.101
−0.06	0.02	6.59×10^{-4}	0.750	−0.04	−0.040	0.101	0.102
−0.06	0.03	1.70×10^{-3}	0.651	−0.031	−0.032	0.103	0.104
−0.06	0.04	3.71×10^{-3}	0.542	−0.022	−0.021	0.104	0.106
−0.06	0.05	6.80×10^{-3}	0.443	−0.013	−0.011	0.105	0.108
−0.14	0	1.81×10^{-8}	0.965	−0.14	−0.14	0.1	0.1
−0.14	0.02	2.19×10^{-7}	0.955	−0.120	−0.121	0.101	0.101
−0.14	0.05	6.45×10^{-6}	0.928	−0.092	−0.093	0.105	0.104
−0.14	0.1	6.42×10^{-4}	0.763	−0.048	−0.050	0.11	0.113
−0.14	0.15	1.00×10^{-2}	0.402	−0.01	0.001	0.116	0.125
−0.14	0.2	2.88×10^{-2}	0.220	0.027	0.053	0.12	0.132
−0.25	0.2	1.11×10^{-4}	0.865	−0.07	−0.095	0.111	0.122
−0.25	0.23	6.43×10^{-4}	0.771	−0.048	−0.071	0.11	0.131
−0.25	0.3	9.37×10^{-3}	0.443	−0.013	0.008	0.12	0.153

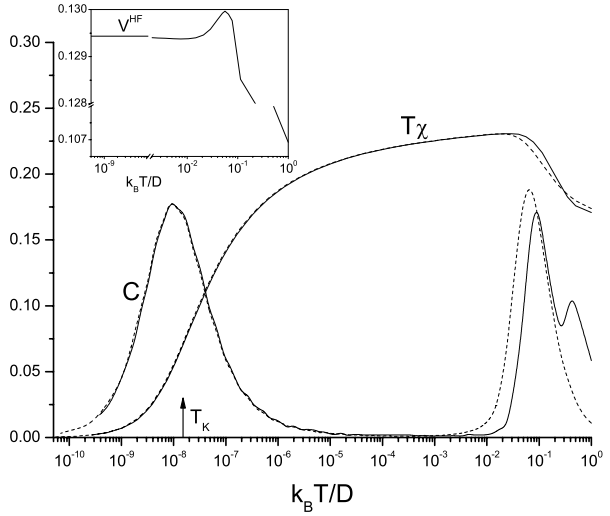

Fig. 4. The quantity $k_{\rm B}T\chi(T)/(g\mu_{\rm B})^2$ and specific heat $C(T)/k_{\rm B}$ for $E_f = -0.5$, $V = 0.1$, $G = 0.4$ (solid) and $E_f^{(G=0)} = -0.14$, $V^{(G=0)} = 0.1$, $G = 0$ (dotted). With these parameters, $n_f = 0.96$ at $T = 0$. The inset shows $V^{\rm HF}(T)$ plotted against $k_{\rm B}T/D$.

model (with $G = 0$) that give the same values of n_f (at zero temperature) and $T_{\rm K}$, as our Hamiltonian (1). A comparison of the present results with those for the model with $G = 0$, and with the effective parameters introduced above shows that for the susceptibility the effects of G in the temperature dependence are nearly eliminated by the parameter renormalization (see Fig. 4). However, weak oscillations at the same temperatures where the changes in the specific heat $C(T)$ take place.

More generally, this elimination is possible for $C(T)$ at sufficiently low temperatures, $T \lesssim T_{\rm K}$. This means that the Wilson ratio is not influenced by the d-f interaction at $T \leq T_{\rm K}$, but its dependence on temperature at higher temperatures is different when $G = 0$ and $G \neq 0$. Naturally, it is expected that the d-f Coulomb (but not exchange) interaction is less important for the magnetic susceptibility than for the specific heat. The former is connected with only spin degrees of freedom, while the latter characterizes *both* spin and charge fluctuations.

Exciton effects are responsible for the enhancement of the double-peak structure at high temperatures for $C(T)$. This behaviour becomes stronger with increasing G (see Fig. 2). Also, charge (valence) fluctuations increase, resulting in a further deviation of valence from an integer value (e.g., $n_f = 0.87$ for $G = 0.2$ and $n_f = 0.77$ for $G = 0.23$). Note that when G is sufficiently large, the metal-insulator transition occurs in the Falicov-Kimball model. This is similar to the Mott-Hubbard transition [26]. It is accompanied by a spectral density transfer, and the formation of so-called "Hubbard bands" in the electron energy spectrum.

To exclude systematic errors, the calculations are repeated using the same model parameters as previously in Figure 2, except with $\Lambda = 1.5$ instead of $\Lambda = 2$: see Figure 5. Recall that the band discretization error decreases when $\Lambda \to 1$. The influence of the Falicov interaction on $C(T)$ is nearly the same, thus demonstrating that the change in specific heat is not an artifact of the method.

Figure 6 shows the magnetic impurity entropy $S(T)$ calculated directly using $G = 0$ and $G = 0.4$. The calculation of this quantity is more precise than $C(T)$ since differentiation with respect to T is not required. At high temperatures $S(T) \to \ln 3 = 1.0986$ since at the limit of large-U, the impurity has three degrees of freedom. At lower temperatures the dependence $S(T)$ demonstrates crossovers and points of inflection which correspond to maxima in $C(T)$. Similar to the other properties, the effect on these features is stronger for finite G. At higher

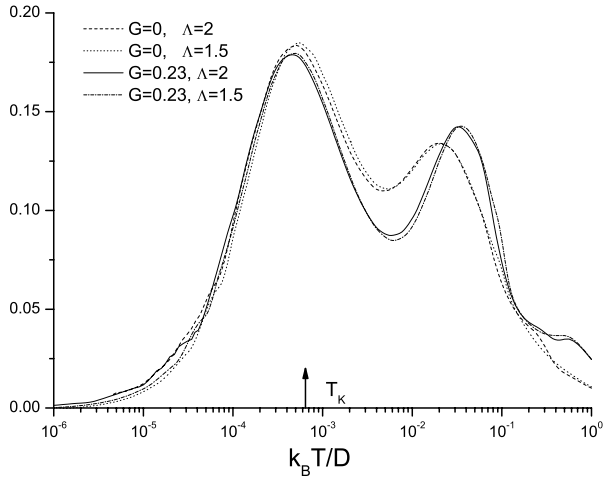

Fig. 5. The specific heat $C(T)/k_{\rm B}$ using the same model parameters as in Figure 2 except for Λ, to show the effect of reducing this parameter from 2 to 1.5.

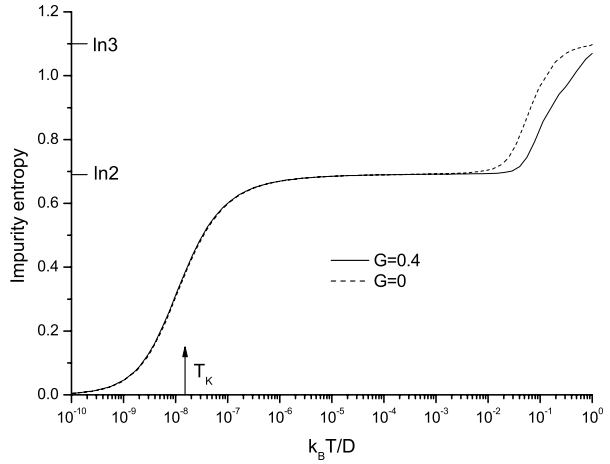

Fig. 6. The magnetic impurity entropy using the same model parameters as in Figure 4.

temperatures, there is clearly a difference between the results for $G = 0$ and $G = 0.4$. Although this is only modest for $S(T)$ (and $T\chi(T)$), it is significantly greater following differentiation with respect to T when calculating $C(T)$.

Recently, a method has been proposed to include the effects of the Falicov-Kimball interactions into realistic electronic structure calculations for intermediate valence systems [10]. In particular, it is shown that these effects are crucial for an adequate description of the equation of state for elemental Yb under high pressure. In reference [10], these effects are taken into account using the unrestricted Hartree-Fock approximation [9],

$$E_f^{\rm HF} = E_f + G\sum_\sigma \langle c_\sigma^\dagger c_\sigma\rangle, V^{\rm HF} = V - G\langle c_\sigma^\dagger f_\sigma\rangle. \qquad (4)$$

Therefore, it is important to check this approximation using the accurate NRG results obtained here. A comparison of the parameters of the effective Anderson model with the Hartree-Fock values (4), which are presented in the Table 1, shows that this approximation works well, at least when the d-f interaction is not too large ($G < 0.25$). The HF mean-field decoupling is also justified by the d-f Coulomb interaction being marginal [12]. The inset in Figure 4 shows $V^{\rm HF}(T)$ plotted against $k_{\rm B}T/D$. In the Kondo regime it can be seen that a maximum occurs which is qualitatively similar to the result of calculations employing the poor-man's scaling formalism [18]. However, it is considerably smaller than that predicted in reference [18].

The significant temperature dependence of the effective hybridization has other important consequences. It is expected that thermodynamical averages at different temperatures will correspond to *different* effective Anderson models. Our NRG calculations confirm that the Falicov model coincides with an Anderson model at low temperatures where the hybridization parameter tends to a definite constant limit. However, a shift to higher temperatures of the second maximum in specific heat occurs, together with the corresponding peculiar feature in the magnetic susceptibility (see in particular Fig.s 4 and 6). This demonstrates that there is a temperature-dependent renormalization of the effective parameters, since such a shift occurs when E_f or $|V|$ increases.

To conclude, an accurate NRG solution is obtained of the one-impurity Anderson model with inclusion of the Falicov-Kimball interaction (excitonic effects). Some new features in comparison with the standard Anderson model occur (in particular, in the temperature dependence of specific heat). These features can be observed experimentally from measurements of specific heat and magnetic susceptibility at high temperatures, and comparison with the "universal" dependences. Such investigations could clarify the role of charge fluctuations in the rare-earth systems under consideration. A generalization of the results to a lattice case would be of interest for the theory of anomalous dense f-systems, including Kondo lattices, heavy fermion, and intermediate valence compounds.

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