Competition between Kondo and RKKY exchange couplings in Pu$_{1-x}$Am$_x$ alloys

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To clarify the role of the Kondo effect in screening local magnetic moments of Plutonium 5f–electrons as well as its competition to the RKKY interactions we use a combination of density functional theory with static Hartree Fock and dynamic Hubbard 1 approximations to calculate the strength of both the Kondo exchange, $J_K$, and of the RKKY exchange, $J_{RKKY}$, couplings for Pu$_{1-x}$Am$_x$ system as a function of $x$. We find that $J_K$ increases despite the atomic volume gets larger with the Am doping due to unexpected enhancement of hybridization between $f$ and conduction electrons in the vicinity of the Fermi level. At the same time, the RKKY exchange is shown to reduce smoothly with increasing $x$. Our results imply that the Kondo effect should be robust against the increase in interatomic spacing of this alloy.

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Magnetic behavior of metallic Plutonium is a topic of hot debates in the current literature. Naively one expects that Pu f–shell filled with 5 electrons carries a total (spin+orbital) momentum which depending on various spin–orbit coupling schemes and crystal field effects should result in some non–zero values of magnetic moment. This has been confirmed by many state–of–the–art electronic structure calculations [2, 3, 4, 5] based on density functional theory (DFT) in its local density and by methods such as LDA+U [7, 8] allowing to incorporate effects of on–site correlation energy [9]. Continuous–Time Quantum Monte Carlo (CT–QMC) method for the solution of impurity problem [19] have detected that at volumes of the order of 30% larger than the volume of the fcc δ–phase the temperature behavior of spin susceptibilities turns from Pauli–like to Curie–like. To simulate similar stretch experimentally, Pu$_{1-x}$Am$_x$ alloys have been made, which, however, on the basis of magnetic susceptibility, electrical resistivity, and photo–electron spectroscopy studies [21, 22, 23], indicated that the character of the 5f states does not vary with the Am doping. This came into a contradiction with the DFT based study of this system [24].

We thus see that deducing the behavior of the Kondo exchange energy as a function of $x$ is an interesting theoretical problem which may shed a light on the description of the recent experimental results in the Pu–Am alloy. As a minimal model applicable for this description is the model of the Kondo lattice, it is also interesting to understand an approximate location of this system in the Doniach phase diagram [25] where the competition between Kondo and RKKY interactions may lead to exciting phenomena of quantum criticality and exotic superconductivity. This, for example, is seen in a different class of Pu–based 115 materials such as PuCoGa$_5$ and PuRhGa$_5$ [26].

In the present work, both the Kondo coupling strength, $J_K$, and the hypothetical magnetic interaction strength, $J_{RKKY}$, are calculated and compared against each other as a function of $x$ using supercell based electronic structure framework where the $f$–electrons are treated as localized. To deduce $J_K$ we measure the hybridization between the $f$ level and the Fermi surface $sd$ electrons. To
deduce $J_{RKKY}$, we use a newly developed linear response approach [27] based on magnetic force theorem [28]. The $f$-electron self-energies are approximated by their atomic Hartree–Fock values using the LDA+U method but the results are checked against the LDA+DMFT calculations with the self-energies extracted by exact diagonalizing many-body atomic Hamiltonians [29].

The main finding of our work is an unexpected increase of $J_K$ with Am doping due to a particular behavior of the hybridization function in the vicinity of the Fermi level and simultaneous decrease of $J_{RKKY}$. The latter is expected as we scale up the interatomic distances of the lattice. Our calculation shows that $J_K$ always remains larger than $J_{RKKY}$ assuming that the Kondo effect is robust against doping transformations from the Kondo lattice to the diluted impurity limit. It also places this system into the heavy fermion region of the Dzialoshinskii phase diagram away from the impurity limit.

In order to estimate the strength of the Kondo coupling we calculate the hybridization function between the $5f$ and the conduction states, $\Delta_{\alpha\beta}(\omega)$, which is generally expressed via the local Green function for the $f$-electrons as follows [18]

$$\Delta_{\alpha\beta}(\omega) = \omega o_{\alpha\beta} - \epsilon_{\alpha\beta} - G_{\alpha\beta}^{-1}(\omega) + \Sigma_{\alpha\beta}(\omega)$$  \hspace{1cm} (1)

where

$$G_{\alpha\beta}(\omega) = \sum_{\mathbf{k}} (\omega \hat{\Omega}_k - \hat{H}_k - \Delta \Sigma(\omega))^{-1}_{\alpha\beta}$$  \hspace{1cm} (2)

Here $\hat{H}_k, \hat{\Omega}_k$ are single particle LDA Hamiltonian and overlap matrix written in a general non-orthogonal LMTO orbital basis while $\Delta \Sigma(\omega)$ is the self-energy correction included in the $f$-electron block only with the double counting potential subtracted. The matrix of impurity levels $\epsilon_{\alpha\beta}$ and the average overlap integrals $o_{\alpha\beta}$ can be found straightforwardly from $\hat{H}_k, \hat{\Omega}_k$ [18].

We utilize the static Hartree Fock approximation for the self-energy by forcing antiferromagnetically ordered state. This is done to keep the same level of accuracy with our subsequent evaluations of the RKKY interactions. We benchmarked these calculations against the Hubbard 1 approximation [29] assuming magnetically disordered solutions and find similar results. Both methods do not assume DMFT self-consistency with respect to the hybridization function and are reduced to the self-consistent determination of charge densities similar to the Kohn–Sham procedure in DFT. The imaginary part of the hybridization function taken at zero frequency determines the strength of the Kondo exchange according to a simple estimate [30]

$$J_K = \frac{Tr\{Im\Delta(0)\}}{\pi N_d N(0)} \frac{U}{\epsilon_f(\epsilon_f + U)}$$  \hspace{1cm} (3)

where $N_d$ is the corresponding degeneracy of the model, $N(0)$ is the density of states at the Fermi level, and $\epsilon_f = Tr\{\epsilon\}/N_d$. Thus we see that all the parameters in this expression can be evaluated in our calculation where we find that the average position of the impurity level $\epsilon_f \approx 1$ eV and the total density of states $N(0) \approx 1.5$ states /eV-atom at the Fermi level are weakly dependent functions of Am concentration, and the trend in $J_K$ is mainly determined by the behavior of $Im\Delta(0)$.

Figure 1 illustrates our calculated behavior of $Tr\{Im\Delta(\omega)\}/N_d \pi$ for frequencies around the Fermi level and for doping levels $x \leq \frac{1}{2}$ assuming full degeneracy $N_d = 14$. Three various lines correspond to the dopings with $x = 0, \frac{1}{3},$ and $\frac{1}{2}$. The following conclusions can be derived. First, all curves look very similar although there is an almost rigid shift of the order of 0.4 eV which separates the calculated $Im\Delta(\omega)$ for various $x$. Second, we monitor the overall trend of decreasing the hybridization between the $f$ and conduction electrons with the
Am doping as one can trace the maximum of each plot. This is easily understood since interatomic distances get larger. However, importantly that for all doping ratios, \(Im \Delta(\omega)\) has a valley and a hilltop at the right hand side of the valley. For pure Pu, the Fermi level is located close to the dip and it gradually climbs up to the hilltop as \(x\) increases. This results in an unexpected increase in hybridization for \(\omega = 0\): \(Tr\{Im \Delta(0)\}/N_d \pi = 0.05\) eV for \(x = 0\); but jumps to 0.10 eV for \(x = \frac{1}{2}\). (see Table I for full compilation of the data). Accordingly, \(J_K\) also increases because \(N(0)\) remains approximately the same for all \(x\) values. If one sets \(N_d = 14\) in Eq. \(3\), then for pure Pu, \(J_K\) is 340 K but becomes 660 K for \(x = \frac{1}{2}\) and further raises to 770 K for \(x = \frac{3}{4}\). Then \(J_K\) decreases but is still sufficiently large as \(x\) approaches the dilute impurity limit. One thus concludes that the Kondo screening is the robust effect upon the Am doping which would prevent the Pu moment to appear at all \(x\) .

As the description in terms of the Kondo lattice Hamiltonian may be relevant for Pu\(_{1-x}\)Am\(_x\) system, its properties should be controlled by the competitions between the Kondo and RKKY exchange interactions which, according to the Doniach phase diagram, depending on the precise value of \(J_K\) may lead to either weakly coupled magnetically ordered local moment state or to the Kondo screened heavy fermion state in the strong coupling limit. It can even put the system in the vicinity of quantum critical point where exotic superconductivity is believed to occur. In the approximation when only a single conduction band hybridizes with the \(f\)-level, \(J_{RKKY}\) scales simply as \(J_K^2 \pi N(0)\) as seen by using the second–order perturbation theory for the Coqblin–Schrieffer Hamiltonian. It may therefore be expected at first glance that both \(J_{RKKY}\) and \(J_K\) should behave similarly upon doping. However, in realistic situations detailed electronic structure of the material matters as various interband transitions contribute to exchange processes and this simple trend may be violated.

In order to estimate the strength of the magnetic interaction between localized 5f states appeared while mapping the Pu sublattice onto the Heisenberg (pseudo)spin Hamiltonian, \(H = \sum_{RR'} J_{RR'} S_R \cdot S_{R'}\) we utilize the magnetic force theorem within a rigid spin perturbation method. In this framework, \(J_{RR'}\) is given as a second–order derivative of the total energy induced by the rotations of magnetic moments at sites \(R\) and \(R'\) which can be found by calculating the following spin–susceptibility–type integral:

\[
J_{\alpha\beta}^{RR'} = \frac{\partial^2 E}{\partial \phi_\alpha R \partial \phi_\beta R'} = \sum_{\mathbf{k} \mathbf{q}} \sum_{\mathbf{j} \mathbf{j}'} f_{\mathbf{k} \mathbf{j}} - f_{\mathbf{k} + \mathbf{q} \mathbf{j}'} \left\langle \mathbf{k} \mathbf{j} \left| \sigma \times \mathbf{B}_R \right| \mathbf{k} + \mathbf{q} \mathbf{j}' \right\rangle \times \left\langle \mathbf{k} + \mathbf{q} \mathbf{j}'' \left| \sigma \times \mathbf{B}_{R'} \right| \mathbf{k} \mathbf{j} \right\rangle e^{i\mathbf{q} \cdot (\mathbf{R} - \mathbf{R}')},
\]

Here \(f_{\mathbf{k} \mathbf{j}}\), \(\sigma\), and \(\mathbf{B}_R\) are the Fermi function, Pauli spin matrix, and the effective magnetic field at atom \(R\), respectively. The latter is given by the difference in the electronic self–energies for spin up and spin down electrons. Since the LDA+U method is employed to recover antiferromagnetically ordered state, those become frequency independent matrices and the evaluation of interatomic exchange interactions is straightforward. In practical calculations using the supercells the total number of nearest neighboring \(J_i\)’s are different for different doping ratios, and we take average values after calculating all possible nearest \(J_i\)’s.

We find that our calculated \(J_{RKKY}\) exhibits a trend opposite to \(J_K\). It decreases as \(x\) increases as it is evident from Table I. The \(J_{RKKY}\) in pure Pu \((x = 0)\) is smaller than \(J_K\), 134 K, which is reasonable in the sense that it is set by the scale \(J^2_K \pi N(0)\) and that from the experimental standpoint there is no local moment in Pu due to the Kondo screening. However, the behavior is quite different from a simple trend that \(J_{RKKY} \sim J^2_K \pi N(0)\) as \(x = \frac{1}{2}\), \(J_{RKKY} \sim 100\) K, and it becomes 67 K at \(x = \frac{3}{4}\). This must be due to interband transitions presented in Eq. \(2\). The positive sign of \(J_{RKKY}\) refers to the AFM order by the convention in Eq. \(1\) and it is consistent with the assumed AFM ground state.

The comparison of these two quantities, \(J_K\) and \(J_{RKKY}\), provides us with a clear picture for the magnetic properties of Pu\(_{1-x}\)Am\(_x\). It follows that \(J_K\) is always larger than \(J_{RKKY}\) up to \(x = \frac{1}{2}\) which covers up the whole range of the experiments up to now. So, if the Kondo screening works for Pu, it should also work for the alloy. Moreover, the trend is quite suggestive as we approach the dilute limit. While we cannot extract the value of \(J_{RKKY}\) for \(x \geq \frac{3}{4}\) (for \(x = \frac{4}{3}\) there is only 1 Pu atom left in our supercell producing FM solution), the overall trend for \(J_{RKKY}\) to decrease is expected as the inter–Pu distances increase. It is therefore clear that \(J_{RKKY}\) would decrease further as \(x\) approaches to unity. The behavior of \(J_K\) for large \(x\) is controlled by \(Im \Delta(0)\) as the Fermi level reaches the vicinity of the top point of the hybridization function as seen in Fig. \(1\). Therefore it begins to decrease slightly at values of \(x \geq \frac{1}{2}\). Nevertheless, even in the dilute impurity limit, where the conduction bands are essentially made of Am sd electrons, our calculated \(J_K\) does not drop sharply as seen from Table I. All this implies that the Pu–Am system is far from the quantum critical behavior and resides in the heavy fermion state.

There are possible sources of errors in our estimates. First, the calculated \(J_{RKKY}\) may be overestimated by

| Am ratio | \(Tr\{Im \Delta(0)\}/14\pi\) | \(J_K\) (K) | \(J_{RKKY}\) (K) |
|----------|-------------------------------|------------|----------------|
| \(x = 0\) | 0.05 | 340 | 134 |
| \(x = \frac{1}{2}\) | 0.10 | 660 | 100 |
| \(x = \frac{3}{4}\) | 0.12 | 770 | 67 |
| \(x = 1\) | 0.10 | 660 | — |

\(x = 0.07\) | 450 | — |
the static approximation, such as LDA+U. This, in particular, was found in the previous studies\cite{27, 38} of transition–metal oxides where the calculated exchange interactions depending on the level of approximation for the self–energy can be further reduced by about 10–30 %.

Second, the use of more refined impurity solvers and corresponding effects of the DMFT self–consistency will change our estimated values of $J_K$, although this effect is not expected to be large due to (i) generally small values in the f–electron hybridization function, and (ii), the position of the f–level at around 1 eV which is pretty far from the Fermi energy preventing the extreme sensitivity of the Kondo temperature. In fact, most recent LDA+DMFT studies of this system based on the CT–QMC method have confirmed these conclusions\cite{39}.

In summary, using a combination of density functional theory with self–energy corrections for the 5f–electrons we performed the estimates of the Kondo and RKKY exchange couplings for the whole range of dopings in Pu$_{1-x}$Am$_x$ alloy. It was found that $J_K$ and $J_{RKKY}$ exhibit opposite trends: the $J_K$ increases with $x$ which is attributed to the details in the behavior of the hybridization function near the Fermi level while $J_{RKKY}$ is found to decrease as interatomic distances get larger with doping. Comparing these two values provides a clear picture of the robust Kondo effect as the origin of non–magnetic behavior reported in recent experiments on this system.

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