Magnetic Fluctuations of Filled Skutterudites
Emerging in the Transition Region between Singlet and Triplet States

Takashi Hotta
Advanced Science Research Center, Japan Atomic Energy Research Institute, Tokai, Ibaraki 319-1195, Japan
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In order to clarify magnetic properties of filled skutterudites, we analyze the Anderson model including seven \( f \)-orbitals hybridized with an \( a_u \) conduction band using a numerical technique. For \( n=2 \) corresponding to Pr-based filled skutterudites, where \( n \) is the local \( f \)-electron number, even if the ground state is a singlet, there remain significant magnetic fluctuations from a triplet state with a small excitation energy. This result can be understood by the fact that \( f \)-electron states are clearly distinguished as itinerant and localized ones in the filled skutterudite structure. This picture also explains the complex results for \( f \)-electron magnetic susceptibility and entropy for \( n=1\sim13 \).

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The recent discovery of heavy fermion superconductivity in \( \text{PrOs}_4\text{Sb}_{12} \) has triggered intensive studies on filled skutterudite compounds in the research field of condensed matter physics. Among the crystalline electric field (CEF) states of filled skutterudites characterized by the \( T_h \) point group, a \( \Gamma_1 \) singlet has been found experimentally to be the ground state of \( \text{PrOs}_4\text{Sb}_{12} \). However, the results of NMR experiments suggest that the superconductivity is unconventional. In fact, \( \text{PrOs}_4\text{Sb}_{12} \) exhibits exotic features such as multiple superconducting phases and the breaking of time-reversal symmetry as detected by \( \mu \)SR experiments. On the other hand, in the same family of \( \text{Pr} \)-based filled skutterudites, \( \text{PrRu}_4\text{Sb}_{12} \) is a conventional \( s \)-wave superconductor, \( \text{PrOs}_4\text{P}_{12} \) is a non-magnetic metal, \( \text{PrRu}_4\text{P}_{12} \) exhibits a metal-insulator transition, and \( \text{PrFe}_4\text{P}_{12} \) shows exotic quadrupolar ordering. It is quite interesting that the electronic properties are easily changed by simple substitution of transition metal atoms and pnictogens.

Besides \( \text{Pr} \)-based filled skutterudites, many other kinds of filled skutterudite compounds have been also synthesized. Those materials also exhibit a variety of electronic properties: \( \text{La} \)-based filled skutterudite materials are known to be conventional BCS superconductors. \( \text{Ce} \)-based filled skutterudites are Kondo semiconductors with energy gaps up to a thousand Kelvins. For skutterudites containing rare-earth ions other than \( \text{La}, \text{Ce}, \text{and Pr} \), a ferromagnetic ground state has been frequently observed, as for instance in \( \text{RFe}_4\text{P}_{12} \) with \( \text{R} = \text{Nd}, \text{Sm}, \text{Eu}, \text{Gd}, \text{Th}, \text{Dy}, \text{and Ho} \). However, antiferromagnetic ground states have also been found in \( \text{GdRu}_4\text{P}_{12} \) and \( \text{TbRu}_4\text{P}_{12} \). It is clearly desirable to identify the key issues which control the electronic properties of filled skutterudite compounds from a microscopic point of view.

However, a microscopic theory for magnetism and superconductivity of \( f^n \)-electron systems with \( n>1 \) (\( n \) is local \( f \)-electron number) has not been satisfactorily developed up to now, owing to the complexity of the many-body problem which stems from the competition among strong spin-orbit coupling, Coulomb interactions, and the CEF effect. To include such interactions, the \( \text{LS} \) coupling scheme has been widely used. However, that approach cannot exploit standard quantum-field theoretical techniques, since Wick’s theorem does not hold in the \( \text{LS} \) coupling scheme. In order to overcome such a difficulty, we have proposed to construct a microscopic model for \( f \)-electron systems based on a \( j-j \) coupling scheme. When we attempt to apply the latter model to filled skutterudites, there are several issues to be addressed. In particular, one may have doubts about the application of the \( j-j \) coupling scheme to rare-earth materials, since Coulomb interactions are generally larger than the spin-orbit coupling in \( 4f \)-electron systems. It is also necessary to clarify how the CEF energy levels for \( f^n \)-electron systems are reproduced in the \( j-j \) coupling scheme.

In this Letter, we analyze a multi-orbital Anderson model, which correctly contains spin-orbit coupling, Coulomb interactions, and the CEF effect. For \( n=2 \), significant magnetic fluctuations are found to remain even in an \( f^2 \)-electron system with a \( \Gamma_1 \) singlet ground state, since there is a \( \Gamma_2^\text{\( 4 \)}} \) excited state triplet with a small excitation energy controlled by the CEF interaction. It is also shown that essentially the same result is obtained in an Anderson model constructed with the \( j-j \) coupling scheme. We find that in filled skutterudites, a certain \( f \) orbital hybridizes with the conduction band, while other orbitals are localized. This picture also explains the magnetic properties of filled skutterudites for \( n=1\sim13 \).

The Anderson Hamiltonian is written as

\[
H = \sum_{k\sigma} \varepsilon_k c_{k\sigma}^\dagger c_{k\sigma} + \sum_{k\sigma m} (V_m c_{k\sigma}^\dagger f_{m\sigma} + \text{h.c.}) + H_I, \tag{1}
\]

where \( \varepsilon_k \) is the conduction electron energy dispersion, \( c_{k\sigma} \) is the annihilation operator for conduction electrons with momentum \( k \) and spin \( \sigma \), \( \sigma = +1 \) (−1) for up (down) spin, \( f_{m\sigma} \) is the annihilation operator for \( f \)-electrons with spin \( \sigma \) and angular momentum \( m(=-3,\cdots,3) \), and \( V_m \) is the hybridization between \( f \) electrons and the conduction band. In filled skutterudites, the conduction band is given by \( a_u \), constructed from \( p \)-orbitals of the pnictogens.
The matrix elements are given by $\zeta^{B}_{m,m'}$ where $\frac{1}{2}$ of the bandwidth of the conduction band [13]. To specify the CEF scheme and scale for the CEF potential, we set $\zeta^{A} = \zeta^{B} = 0$, $\zeta^{C} = \zeta^{D} = 0$, and $\zeta^{T} = 0$. Note that hybridization occurs between states with the same symmetry. Since the $d_{x^2-y^2}$ conduction band has $xyz$ symmetry, we set $\zeta^{B} = \zeta^{A} = 0$, $\zeta^{C} = \zeta^{D} = 0$, and $\zeta^{T} = 0$. This leaves the $x$ and $y$ components of the conduction electrons free to hybridize. The Coulomb integral $I$ is given by 

$$I = \sum_{m,\sigma,m',\sigma'} f_{m\sigma}^\dagger f_{m'\sigma'},$$

where $B_{m,m'}$ is the CEF potential for angular momentum $l = \frac{3}{2}$, $\delta_{\sigma\sigma'} = (1 + \sigma \sigma')/2$, $\lambda$ is the spin-orbit coupling. The matrix elements are given by $\zeta_{m,m',m',\sigma} = m\sigma/2$, $\zeta_{m+1,m,m,\pm 1} = \sqrt{12 - m(m \pm 1)/2}$, and zero for the other cases. The Coulomb integral $I_{m_1,m_2,m_3,m_4}$ is expressed by the combination of four Racah parameters, $A$, $B$, $C$, and $D$. For the $T$ point group, $B_{m,m'}$ is given by three parameters, $x$, $y$, and $W$, where $x$ and $y$ specify the CEF scheme and $W$ denotes the energy scale for the CEF potential.

Let us first examine the local $f$-electron states, in order to set the parameters and check the validity of $H$. In Fig. 1(a), eigen-energies of $H$ in the low-energy region are plotted as functions of $x$ for $n=2$. The other CEF parameters, Racah parameters, and the spin-orbit interaction are appropriately chosen for filled skutterudites. It is observed that the results for the LS coupling scheme are well reproduced, but we also emphasize that $H_l$ correctly reproduces the local $f$-electron states for both the LS and $j$-$j$ coupling schemes, depending on the Coulomb interactions and spin-orbit coupling, for any value of $n$. Recall that the $\Gamma_1$ singlet ground state and $\Gamma_{4}^{(2)}$ triplet excited state are split by only a small energy difference in Pr-based filled skutterudites [13]. To study this, we magnify the region in which the $\Gamma_1$ and $\Gamma_{4}^{(2)}$ states cross. In the following, we consider the region in Fig. 1(b) where $0.36 \leq x \leq 0.37$.

Here we include the hybridization between $f$ electrons and conduction band states. For this purpose, we employ the numerical renormalization group (NRG) method [15], in which the momentum space of the conduction electrons is logarithmically discretized near the Fermi energy. The discretization is determined by a cut-off parameter $\Lambda$. In this paper we use $\Lambda=5$. Due to the limitation of computer memory, we keep only 4000 low-energy states for each renormalization step, but the results do not change qualitatively for $\Lambda \geq 3$ when 4000 states are kept.

In order to examine the properties of the $f$ electrons, we evaluate the magnetic susceptibility $\chi$ and the entropy $S$ of the $f$ electrons. In Fig. 2(a), we show calculated results for $T \chi$ for $n=2$ and several values of $x$ between 0.36 and 0.37. For $x \leq 0.365$, $T \chi$ goes to zero for small $T$, while for $x \geq 0.366$, $T \chi$ becomes constant at low temperatures [14]. As shown in Fig. 2(b) for $S$, we obtain $\log 3$ as a residual entropy for $x=0.366$ and 0.37, indicating that a local triplet remains in the low-temperature region. Here we emphasize that magnetic fluctuations still remain at low temperatures, even when $\Gamma_1$ is the ground state, if $\Gamma_{4}^{(2)}$ is an excited state with a small excitation energy. We suspect that anomalous properties of Pr-based filled...
skutterudites originate from such magnetic fluctuations. We remark that the transition between magnetic and non-magnetic states is governed by the exchange interaction \(J_{\text{ex}}\) between \(f\)-electrons and the conduction band, expressed as \(J_{\text{ex}}=V^2/\delta E\), where \(\delta E\) denotes the energy difference between the \(f^2\) and \(f^3\) (or \(f^4\)) lowest-energy states. As shown in Fig. 2(c), the boundary curve between magnetic and non-magnetic phases is proportional to \(V^2\), suggesting that the dominant energy scale should be \(J_{\text{ex}}\) for the appearance of magnetic fluctuations.

Note that the transition between magnetic and non-magnetic states seems to be abrupt, not gradual as observed in the usual Kondo system and the two-channel Anderson model \(17\). In the Kondo problem, the local moment is suppressed only by hybridization with conduction electrons, but in the present case, a singlet ground state is also obtained through local level crossing due to the CEF potential, in addition to the hybridization process. Furthermore, localized orbitals exist in the present model, as will be discussed later. Namely, the magnetic moments of the \(f\) orbitals hybridized with the conduction band are suppressed as in the Kondo effect, while the moments of the localized orbitals are not screened \(18\). An abrupt change in the magnetic properties is caused by the duality of the \(f\) orbitals in combination with the level crossing effect due to the CEF potential.

In order to understand the above point more explicitly, it is useful to express the \(f\)-electron state with \(xyz\) symmetry in the \(j-j\) coupling scheme as

\[
|\text{xyz}, \sigma\rangle = \sqrt{4/7}|7/2, \tilde{\Gamma}_7, \tilde{\sigma}\rangle - \sqrt{3/7}|5/2, \tilde{\Gamma}_7, \tilde{\sigma}\rangle,
\]

where \(|j, \tilde{\Gamma}, \tilde{\sigma}\rangle\) denotes the state in the \(j-j\) coupling scheme with total angular momentum \(j\), irreducible representation \(\tilde{\Gamma}\) for the \(O_h\) point group \(19\), and pseudospin \(\tilde{\sigma} = 20\). This relation indicates that only the \(\tilde{\Gamma}_7\) state is hybridized with the \(a_{\text{co}}\) conduction band states with \(xyz\) symmetry, leading to the Kondo effect, while the \(\tilde{\Gamma}_8\) electrons are localized and become the source of local fluctuations at low temperatures. It is an important issue of filled skutterudite structures that the nature of the \(f\) electrons can clearly be distinguished as itinerant \(\tilde{\Gamma}_7\) or localized \(\tilde{\Gamma}_8\). This point provides a possible explanation for the heavy-fermion phenomenon occurring in \(f^7\)-electron systems such as Pr-based filled skutterudites.

In the \(j-j\) coupling scheme, the model is rewritten as

\[
\hat{H} = \sum_{k\sigma} E_k a_{k\sigma}^\dagger a_{k\sigma} + \sum_{k\sigma}(V a_{k\sigma}^\dagger f_{\sigma\tilde{\sigma}} + \text{h.c.}) + \hat{H}_1,
\]

where \(E_k\) is the dispersion of the \(\tilde{\Gamma}_7\) conduction electrons, \(a_{k\sigma}\) is the annihilation operator for conduction electrons with momentum \(k\) and pseudospin \(\tilde{\sigma}\), \(f_{\sigma\tilde{\sigma}}\) is the annihilation operator for \(f\) electrons with pseudospin \(\tilde{\sigma}\) and orbital \(\gamma\) for the \(j=5/2\) sextet on the impurity site, and \(V\) is the hybridization between conduction and \(f\) electrons with \(\tilde{\Gamma}_7\) symmetry. The orbital index \(\gamma\) distinguishes three kinds of Kramers doublets, two \(\tilde{\Gamma}_8\) (\(a\) and \(b\)) and one \(\tilde{\Gamma}_7\) (\(c\)). The local \(f\)-electron term \(\hat{H}_1\) is given by

\[
\hat{H}_1 = \sum_{\gamma, \sigma} f_{\gamma\sigma}^\dagger f_{\gamma\sigma} + (1/2) \sum_{\gamma_1=\gamma_4, \sigma_1, \sigma_2} f_{\gamma_1, \gamma_2, \gamma_3, \gamma_4}^\dagger f_{\gamma_1, \gamma_2, \gamma_3, \gamma_4} f_{\gamma_2, \gamma_3, \gamma_4, \sigma_1},
\]

where \(\tilde{\Gamma}_7\) is the CEF potential and \(\hat{I}\) is the Coulomb interaction in the \(j-j\) coupling scheme, expressed by other Racah parameters \(E_0, E_1,\) and \(E_2\). Since the CEF potential is already diagonalized, it is convenient to introduce a level splitting \(\triangle\) between \(\tilde{\Gamma}_7\) and \(\tilde{\Gamma}_8\) as \(\Delta = \tilde{B}_{\tilde{\Gamma}_8} - \tilde{B}_{\tilde{\Gamma}_7}\). In Fig. 2(d), we depict the low-energy states of \(\hat{H}_1\) vs. \(\Delta\) for \(n=2\). The ground state for \(\Delta<0\) is a \(\tilde{\Gamma}_5\) triplet composed of a couple of \(\tilde{\Gamma}_8\) electrons, while for \(\Delta>0\), it is a \(\Gamma_1\) singlet which is mainly composed of two \(\tilde{\Gamma}_7\) electrons. Note that for \(\Delta>0\), the first excited state is a \(\Gamma_4\) triplet composed of \(\tilde{\Gamma}_7\) and \(\tilde{\Gamma}_5\) electrons.

Now we again employ the NRG method to investigate the magnetic properties of the Anderson model in the \(j-j\) coupling scheme. In Figs. 2(e) and (f), we depict \(T\chi\) and \(S\) for several values of \(\Delta\). Racah parameters are set as appropriate values for rare-earth compounds. It is observed that \(T\chi\) becomes constant and residual entropy \(\log 3\) remains at low temperatures for \(\Delta < 5 \times 10^{-5}\), while \(T\chi\) goes to zero rapidly for \(\Delta \geq 6 \times 10^{-5}\). Note that the transition is also dominated by \(J_{\text{ex}}\).

Let us consider the reason why the essential magnetic features of Pr-based filled skutterudites can be captured as described in the \(j-j\) coupling scheme. As shown in Fig. 2(d), when the ground state is a \(\Gamma_1\) singlet, there are two triplet excited states, \(\Gamma_4\) and \(\tilde{\Gamma}_5\). The \(\tilde{\Gamma}_5\) triplet is composed of a pair of \(\tilde{\Gamma}_8\) electrons, while the \(\Gamma_4\) triplet is composed of one \(\tilde{\Gamma}_7\) and one \(\tilde{\Gamma}_8\) electron. Since \(\tilde{\Gamma}_8\) electrons do not hybridize with \(\tilde{\Gamma}_7\) conduction electrons, the \(\tilde{\Gamma}_5\) triplet can survive. Note that \(\Gamma_4\) triplets in \(T_h\) are given by the mixtures of \(\Gamma_4\) and \(\Gamma_5\) in \(O_h\). Such a mixing is not included in the \(j-j\) coupling scheme, but there is a \(\tilde{\Gamma}_5\) excited state. Thus, the local triplet still remains, as long as the excitation energy is smaller than \(J_{\text{ex}}\).

Thus far, we have focused on the case of \(n=2\), but we can further study the cases of \(n=1\sim 13\) based on the original Anderson model \(11\). In the point-charge picture, the CEF parameters do not depend on \(n\), since the CEF effect is due to electrostatic potential from ligand ions surrounding the rare earth. In the following, we fix \(z=0.366\), in which the local \(f^2\) ground state is a \(\Gamma_1\) singlet, but for which we have found significant magnetic fluctuations at low temperatures. In Figs. 3(a) and (b), the magnetic susceptibility and entropy for each case of \(n=7\) are shown. For \(n=2\), 4, and 6, the ground state is a \(\Gamma_1\) singlet. Except for the case of \(n=2\), the excitation energy is large and both magnetic and orbital fluctuations should be rapidly suppressed with decreasing temperature. Thus, \(T\chi\) immediately becomes zero at low temperatures for \(n=4\) and 6. On the other hand, for \(n=1\),
3, and 5, the ground state is a $\Gamma_7$ quartet in $T_h$ ($=\tilde{\Gamma}_8$ in $O_h$), as confirmed from the residual entropy of $\log 4$.

In Figs. 3(c) and (d), we show the NRG results for susceptibility and entropy for $n\geq 7$. First of all, the absolute values of $\chi$ are much larger than those for $n<7$, since the total angular momentum $J$ becomes large for $n\geq 7$ owing to Hund’s rule coupling. Typically, at half-filling, total spin $S(=J)$ is equal to 7/2, and the Curie constant for an isolated ion is as large as $21\mu_B^2/k_B$. Over a broad temperature region, this value has been observed in Fig. 3(c) for $n=7$, indicating that the $S=7/2$ spin survives at relatively low temperatures. In fact, we clearly see an entropy of $\log 8$ from the $S=7/2$ octet, as shown in Fig. 3(d).

For the cases of $n=8$ and 12, the ground state is a $\Gamma_1$ singlet and the magnetic excited state energy is now large, in sharp contrast with the case of $n=2$. Thus, the susceptibility rapidly goes to zero. For $n=9, 11$, and 13, the local ground state is a $\Gamma_5$ doublet in $T_h$ ($=\Gamma_8$ in $O_h$). Thus, this state does not hybridize with the conduction band and the magnetic moment still persists even in the low-temperature region. In fact, we observe a residual entropy of $\log 2$ in these cases, as shown in Fig. 3(d). For $n=10$, the local ground state is a $\Gamma_4$ triplet, but as observed in Figs. 3(c) and (d), the local triplet seems to remain at low temperatures. This is easily understood, if we recall that $\Gamma_4$ triplets of $T_h$ are given by mixtures of $\tilde{\Gamma}_4$ and $\tilde{\Gamma}_5$ of $O_h$. As mentioned above, the $\tilde{\Gamma}_5$ triplet still persists even after hybridization, since a $\tilde{\Gamma}_8$ electron does not hybridize with a $\tilde{\Gamma}_7$ conduction electron.

In summary, we have analyzed a multi-orbital Anderson model using the NRG method. We have established that $\tilde{\Gamma}_7$ states hybridize with the conduction band, while $\tilde{\Gamma}_8$ states are localized. For $n=2$, corresponding to Pr-based filled skutterudites, it has been found that magnetic fluctuations significantly persist, if there is a $\Gamma_4^{(2)}$ excited state triplet with a small excitation energy. It has been shown that essentially these same results are reproduced by the Anderson model in the $j-j$ coupling scheme. We believe that these results open a new door for the study of magnetic and superconducting properties of Pr-based filled skutterudites from a microscopic point of view.

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[19] In the $j-j$ coupling scheme, we use the notation for $O_h$, since the CEF potential for one $f$-electron state in the $j=5/2$ sextet is the same for $O_h$ and $T_h$. See also Ref. 2.
[20] There is one-to-one correspondence between $\sigma$ and $\tilde{\sigma}$.
[21] At extremely low temperatures, however, $S=7/2$ spin seems to be eventually screened and only $S=1/2$ remains, leading to the residual entropy $\log 2$. 

FIG. 3: (a) Magnetic susceptibility and (b) entropy of $f$ electrons vs. $T$ for $n=1$–6. (c) Magnetic susceptibility and (d) entropy for $n=7$–13. We set $x=0.366$ and all other parameters are the same as those in Figs. 2 (a) and (b).