Magnetically Robust Multipole Kondo Effect

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Abstract. In order to promote our understanding on magnetically robust heavy-fermion phenomenon observed in Sm-based filled skutterudites, we focus on Kondo-like behavior due to multipole degree of freedom. By employing a numerical renormalization group method, we evaluate the Sommerfeld coefficient $\gamma$ of electronic specific heat of a seven-orbital Anderson model with five $f$ electrons corresponding to Sm$^{3+}$ ion under a magnetic field $H$. From the numerical results, we discuss the dependence of $\gamma$ on $H$ for $(0, 0, 1)$, $(1, 1, 0)$, and $(1, 1, 1)$ directions. It is observed in common that $\gamma$ is eventually independent of $H$ for large magnitude of $H$. Note, however, that for $(1, 1, 1)$ direction, we find a sharp increase of $\gamma$ around at 11 Tesla, which may be a signal for the relevance of xyz octupole moment.

1. Introduction
Recently, magnetically robust heavy-fermion phenomenon observed in Sm-based filled skutterudites has attracted attention [1], since it will bring a new possibility of electronic state emerging in strongly correlated $f$-electron systems. Concerning the origin of this peculiar phenomenon, the non-magnetic Kondo effect due to electron-phonon interaction has been pointed out [2, 3, 4], since local anharmonic oscillation of rare-earth ion, i.e., rattling motion, in the pnictogen cage has been considered to play important roles for electronic properties of filled skutterudites. In fact, along this research direction, the present author has discussed Kondo effect in an electron system coupled with local Holstein or Jahn-Teller phonon [5, 6, 7, 8, 9, 10]. However, similar magnetically robust heavy-fermion behavior has been also observed in SmFe$_4$P$_{12}$ [11], in which the size of pnictogen cage is smaller than that of SmOs$_4$Sb$_{12}$ and the effect of rattling is not considered to be so significant. Namely, the electron-phonon interaction is not the only possibility to understand magnetically robust heavy-fermion phenomenon in Sm-based filled skutterudites. Then, in parallel with the phonon-based scenario, the present author has proposed an alternative scenario of multipole Kondo effect [12]. Since higher-rank multipoles do not directly couple with the magnetic field, in general, the multipole Kondo effect is not so sensitive to the magnetic field, which may lead to a basic concept to understand magnetically robust heavy-fermion phenomenon.

In this paper, in order to examine the scenario based on multipole Kondo effect, we evaluate the Sommerfeld constant $\gamma$ of the seven-orbital Anderson model under a magnetic field by using a numerical renormalization group (NRG) technique. It is found that $\gamma$ is almost constant for high magnetic field, although $\gamma$ is somewhat decreased when we apply a low magnetic field, since there is non-zero coupling between dipole and higher-rank multipole. We also observe a sharp increase of $\gamma$ for the magnetic field along $(1, 1, 1)$ direction, which is closely related to the state characterized by $\Gamma_{2u}$ octupole moment.
2. Model and Method

The seven-orbital Anderson model under a magnetic field is given by

\[
H = \sum_{k,\sigma} \epsilon_k c_{k\sigma}^+ c_{k\sigma} + \sum_{k,\sigma,m} (V_m c_{k\sigma}^+ f_{m\sigma} + \text{h.c.}) + \sum_{m,m'} B_{m,m'} f_{m\sigma}^+ f_{m'\sigma}
\]

\[
+ \lambda \sum_{m,\sigma,m',\sigma'} \zeta_{m,\sigma,m',\sigma'} f_{m\sigma}^+ f_{m'\sigma} + \sum_{m_1,m_2,m_3,m_4} I_{m_1,m_2,m_3,m_4} f_{m_1\sigma}^+ f_{m_2\sigma} f_{m_3\sigma'} f_{m_4\sigma}
\]

\[
+ \mu_B \sum_{\alpha} \sum_{m,\sigma,m',\sigma'} H_\alpha \left( \ell_{m,m'}^{\alpha} \delta_{\sigma,\sigma'} + 2 s_{\sigma,\sigma'}^{\alpha} \delta_{m,m'} \right) f_{m\sigma}^+ f_{m'\sigma'},
\]

where \( \epsilon_k \) denotes conduction electron dispersion, \( \alpha_\sigma \) indicates the annihilation operator for conduction electron with momentum \( k \) and spin \( \sigma \), \( \alpha = \pm 1 \) (up (down) spin). \( f_{m\sigma} \) denotes the annihilation operator of \( f \) electron, \( m \) is the \( z \)-component of angular momentum \( \ell=3 \), \( V_m \) is the hybridization between conduction and \( f \) electrons, \( B_{m,m'} \) is the crystalline electric field (CEF) potential, \( \lambda \) is the spin-orbit interaction, and the matrix element \( \zeta \) is given by \( \zeta_{m,\sigma,m',\sigma'}=m\sigma/2 \) and \( \zeta_{m+\sigma,-\sigma,m,-\sigma}=\sqrt{(\ell+1)-m(m+\sigma)}/2 \). The Coulomb integral \( I_{m_1,m_2,m_3,m_4} \) is expressed by \( I_{m_1,m_2,m_3,m_4} = \sum_{k=0}^{4} F_k c_k(m_1,m_4)c_k(m_2,m_3) \), where \( F_k \) indicates the Slater-Condon parameter and \( c_k \) is the Gaunt coefficient [13]. Note that the sum is limited by the Wigner-Eckart theorem to \( k=0, 2, 4, \) and \( 6 \). Concerning a magnetic field, we consider only the local magnetic field at an impurity site. Here \( \mu_B \) is a Bohr magneton, \( H_\alpha \) indicates the \( \ell \)-component of the applied magnetic field, \( \ell' \) denotes the \( \ell \)-component of the angular momentum operator for \( \ell=3, s=\sigma/2, \) and \( \sigma' \) indicates the \( \sigma \)-component of Pauli matrices.

The parameters in the model are set as follows: For filled skutterudites, the main conduction band is expressed by \( a_u \), constructed from \( p \)-orbitals of pnictogen [14]. Note that the hybridization occurs between the states with the same symmetry. Since the \( a_u \) conduction band has xyz symmetry, we set \( V_2=-V_2=V \) and zero for other \( m \). The hybridization is fixed as \( V=0.05 \) eV and a half of the bandwidth of \( a_u \) conduction band is set as 1 eV. The CEF potential \( B_{m,m'} \) is expressed by three CEF parameters \( B_0^0, B_0^6, \) and \( B_2^6 \), which are given by \( B_0^0=W x/15, B_0^6=W (1-|x|)/180, \) and \( B_2^6=W y/24 \), respectively [15, 16]. Here we set \( W=-0.4 \) meV, \( y=0.3, \) and \( x=0.3 \) so as to reproduce quasi-quartet CEF scheme of \( \text{PrOs}_4\text{Sb}_12 \) [17, 18, 19]. As for the Slater-Condon parameters, from the fitting of energy spectrum of \( \text{Pr}^{3+} \) ion, we have determined them as \( F_0^0=10 \) eV, \( F_2^2=8.75 \) eV, \( F_3^3=6.60 \) eV, and \( F_6^6=4.44 \) eV [20]. The spin-orbit coupling for \( \text{Sm}^{3+} \) ion is set as \( \lambda=0.144 \) eV [21]. In order to adjust the local \( f \)-electron number \( n_f=5 \) for \( \text{Sm}^{3+} \) ion, we appropriately set the chemical potential. Here we simply assume trivalent state for \( \text{Sm} \), but in actuality, there occurs mixed valence state in some \( \text{Sm} \)-based filled skutterudites. In fact, soft- and hard X-ray spectroscopy has suggested that the energy difference between \( \text{Sm} \) divalent and trivalent states are very small in \( \text{SmOs}_4\text{Sb}_12 \) [22].

In order to analyze the Anderson model, in this paper, we employ a numerical renormalization group (NRG) method [23]. In this technique, we can include efficiently the conduction electron states near the Fermi energy by discretizing momentum space logarithmically. Note that in actual calculations, it is necessary to introduce a cut-off \( \Lambda \) for the logarithmic discretization of the conduction band. Due to the limitation of computer resources, we keep only \( M \) low-energy states. In this paper, we set \( \Lambda=5 \) and \( M=3000 \). We note that a temperature \( T \) is defined as \( T_N=\Lambda^{-(N-1)/2} \) in the NRG calculation, where \( N \) is the number of the renormalization step.

By using the NRG method, we analyze the Sommerfeld constant \( \gamma \), which is the \( T \)-linear coefficient of the expansion in terms of \( T \) in the low-temperature region. Here we calculate \( \gamma \) through the relation of \( \gamma=C/T \) at a low temperature, where \( C \) is the specific heat of \( f \) electron. Namely, it is necessary to obtain \( C \) with high accuracy. For the purpose, we calculate it by the numerical derivative of the entropy \( S \) through the relation of \( C = \partial S/\partial \log T = (S_{N-1} - S_N)/\log(\Lambda^{1/2}) \) [24], where \( S_N \) is the entropy at the step \( N \).
Figure 1. Numerical results of the dependence of the Sommerfeld coefficients on the magnetic field for $\mathbf{H}=(H,0,0)$ (black circles), $(H,H,0)$ (red squares), and $(H,H,H)$ (green diamonds).

3. Result and Discussion

Before proceeding to the numerical results of $\gamma$, let us briefly explain the multipole state of the present model under a magnetic field. As pointed out by the present author [12], for $\mathbf{H}=(H,H,H)$, we observe that $\Gamma_{2u}$ octupole moment is induced, while for $(0,0,H)$ and $(H,H,0)$ directions, $\Gamma_{3g}$ quadrupole moments are found to be induced. Note that only for $\mathbf{H}=(0,0,H)$, $\Gamma_{5u}$ octupole has been found to dominate dipole and $\Gamma_{4u}$ octupole. When we apply a magnetic field, there occurs an entropy release concerning multipole degree of freedom in the low-temperature region, leading to the Kondo-like behavior observed in the peak of the specific heat.

In the present calculations, we evaluate $\gamma$ after the release of entropy concerning multipole degree of freedom. In Fig. 1, we show the dependence of $\gamma$ on the magnetic field $\mathbf{H}$. Black circles, red squares, and green diamonds denote the results for $\mathbf{H}=(0,0,H)$, $(H,H,0)$, and $(H,H,H)$, respectively. It is found that $\gamma$ is almost constant for high magnetic field, except for a sharp peak for $\mathbf{H}=(H,H,H)$ with $H \sim 11$ Tesla. Since there exists non-zero coupling between dipole and higher-rank multipole and such magnetic multipole component is affected by an applied magnetic field, $\gamma$ is somewhat decreased for low magnetic field.

Concerning a sharp peak around at $H \sim 11$ Tesla for $(1,1,1)$ direction, it originates from the change of the local ground state due to a magnetic field. From the results of the local expectation value of the multipole moment [12], we have found that $\Gamma_{2u}$ octupole provides the largest value in the present range of the magnetic field. We have also observed that other large components are $4u$ dipole and $5g$ quadrupoles.

For the case with five $f$ electrons, we have already found that $\Gamma_{2u}$ octupole moment with $xyz$ symmetry becomes dominant, when we assume that $\Gamma_{7}$ and $\Gamma_{8}$ orbitals are itinerant and localized, respectively, as is expected to occur in filled skutterudite materials [25]. In fact, it has been also found that $\Gamma_{2u}$ octupole order appears in the bc lattice structure within the mean-field calculation in the multi-orbital Hubbard model for $f$-electron systems [26, 27]. If it is possible to detect anomalous enhancement of $\gamma$ for the magnetic field along $(1,1,1)$ direction, it may be an evidence of the relevance of $\Gamma_{2u}$ octupole moment to the ground state, in spite of the difficulty to grasp the evidence of $\Gamma_{2u}$ octupole ordering.

In this paper, we have shown the Sommerfeld constant normalized by the value at zero magnetic field, but it seems to be difficult to discuss the absolute value of $\gamma$ from the present calculations, since $\gamma$ is related to the density of states at the Fermi energy, i.e., the bandwidth of conduction electrons, which is a parameter in the present calculation. When we simply assume the conduction electron bandwidth in the order of eV, the value of $\gamma$ is less than 1 mJ/mol·K$^2$, which does not indicate heavy effective mass. However, it has been reported that it is possible to obtain large $\gamma$ in the order of 100 mJ/mol·K$^2$, when we consider the Anderson model coupled with local phonons. In any case, in order to discuss the large absolute value of $\gamma$ within electronic models, it seems to be necessary to analyze the periodic multiorbital Anderson model. It is one of future problems.
4. Summary
We have evaluated the Sommerfeld coefficient for the case of five $f$ electrons on the basis of the seven-orbital Anderson model with the use of the NRG method. We have found that $\gamma$ becomes eventually independent of $H$ for large $H$, although we could not show that $\gamma$ is almost constant even at a low magnetic field. We have observed that $\gamma$ is sharply increased for the magnetic field along $(1,1,1)$ direction, which may be an evidence of the $\Gamma_{2u}$ octupole ordering.

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