Origin of anomalous specific heat coefficient of YbAl$_3$

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Abstract. By using recently proposed effective model for heavy fermion metallic systems, the temperature dependence of the specific heat coefficient of typical heavy fermion material YbAl$_3$ is investigated. The Hamiltonian of the band term consists of the conduction electrons described with nearly free electron method, the localized 4f electrons of Yb ions and the hybridization term between the conduction and 4f electrons. In order to take account of the correlation effect, we reconstruct the low-energy effective Hamiltonian where the low-energy bands near the Fermi level are extracted. The self-consistent perturbation theory with local approximation is applied to this Hamiltonian, so that some physical quantities are calculated. The obtained temperature dependence of the specific heat divided by temperature shows two peak structures, which are in agreement with the experimental results of YbAl$_3$. We show that one peak structure at the very low temperature region originates from the correlation effect and the other peak structure results from the band structure.

1. Introduction
The rare-earth compounds have attracted much interest because of the variety of physical phenomena [1], which have been often investigated by means of the periodic Anderson model (PAM). Although such investigations have succeeded in describing certain physical properties, too much simplification often leads to even qualitatively incorrect results. For example, the neglect of the orbital degeneracy does not describe the appearance of a hybridization gap correctly. Thus, based on the band calculations, the effective models have been constructed. However, it is well known that the band calculation for heavy fermion compounds sometimes reproduces incorrect f-electron level. Recently for the heavy fermion compounds with conduction band composed of s- or p- electrons, we proposed a new method to construct the effective Hamiltonian with realistic band structure [2]. Thus, we can study the rare-earth materials quantitatively from another point of view by means of this technique. In addition to this, our model can capture the basic properties of materials such as lattice symmetry, and various physical quantities can be calculated quantitatively from almost absolute zero to finite temperature region within the desired accuracy in the wave-vector $k$ and frequency $\omega$ spaces. Thus, this model may be good starting point to discuss the physical properties of rare-earth materials with strong correlation.

The effective Hamiltonian for the band term consists of three parts; the conduction electrons are described by nearly free electron method (NFE), localized f electrons and the hybridization between these electrons, in which this model includes only a few parameters. By means of this model Hamiltonian, we investigated the physical properties of YbAl$_3$ [2]. While the eigenvalues are in good agreement with the Local Density Approximation (LDA) result [3] near and below the Fermi level, the Sommerfeld coefficient is 13.5 mJ·K$^{-2}$·mol$^{-1}$, which is underestimated in
comparison with the experimental value ($\sim 40 \text{ mJ}\cdot\text{K}^{-2}\cdot\text{mol}^{-1}$ [4, 5, 6]). It is because the absence of consideration for the correlation effect.

Note here that YbAl$_3$ has Cu$_3$Au-type crystal structure. The mean valence is in the range from 2.65 to 2.8 [7, 8], which indicates YbAl$_3$ is a valence fluctuation material. The single site Kondo temperature $T_K$ is about 500 K [5] and the coherence temperature $T_{coh}$ is 35 K, below which the electric resistivity is proportional to $T^2$ [5, 9]. The Sommerfeld coefficient $\gamma$ is about 40 mJ·K$^{-2}$·mol$^{-1}$. The temperature dependence of the specific heat divided by temperature $c_V(T)/T$ shows two peak structure. With an increase of temperature from absolute zero temperature, $c_V(T)/T$ reduced gradually until $T \sim T_{coh}$. Furthermore, the cusp structure is observed at $T \sim 70\text{K}$.

In the present study, we focus on the specific heat and its temperature dependence of YbAl$_3$ by means of our proposed Hamiltonian.

2. Model and Method

The Hamiltonian $H$ consists of the band term $H_{\text{band}}$ and the interaction term between 4f electrons $H_{\text{int}}$. First, let us review briefly the band term $H_{\text{band}}$ [2]. The electric configuration of each atom of YbAl$_3$ is [Ne](3s)$^2$(3p)$^1$ for Al and [Xe](4f)$^{14}$(5d)$^0$(6s)$^2$ for Yb. Thus there are 25 electrons per unit cell of YbAl$_3$ except the closed shell for each atom. The configuration of 4f electrons lies from f$^1$ to f$^{14}$. The most of conduction electrons are s- or p-electrons, which spread over the crystal on the weak periodic potentials. Thus, we apply NFE method to the conduction electrons. The weak atomic periodic potential is described by the empty-core pseudo-potential, of which core radius and effective valence number are taken from Harrison’s text book [10, 11]. The 14-fold degenerated 4f electron levels split into total angular momentum $J = 7/2$ and $J = 5/2$ because of strong spin-orbit coupling for YbAl$_3$. The $J = 7/2$ level $E_i^{7/2}$ is located near and below the Fermi level $E_F$ where $E_i^{7/2}$ is introduced as a tuning parameter while the $J = 5/2$ level is far from $E_F$. The hybridization term between the conduction and 4f electrons is described by this spherical harmonics because the plane wave with wave-vector $\mathbf{k}$ and the localized 4f electron is expanded by means of the spherical harmonics. We approximate the radial part of the matrix element by constant $V$, which is a tuning parameter, while we still keep the angular dependence of the matrix element. In the present treatment, we stress that the band term of the Hamiltonian contains only a few parameters.

Diagonalizing $H_{\text{band}}$, we can obtain the eigenvalues $E_{k\alpha}$ and rewrite $H_{\text{band}} = \sum_{k\alpha} E_{k\alpha} a_{k\alpha}^\dagger a_{k\alpha}$, where $a_{k\alpha}$ stands for an annihilation operator of a quasi-particle with the wave-vector $\mathbf{k}$ and the band index $\alpha$. These obtained eigenvalues are in good agreement with the LDA result below and near $E_F$ except $M$-point [3].

In order to consider the correlation effect of YbAl$_3$ for the physical quantities, let us discuss the Coulomb interaction term $H_{\text{int}}$, which is assumed as the Hubbard type interaction between 4f electrons. Since the correlation effect between 4f electrons is essential at the low-energy region, we focus on the low-energy region near $E_F$. Thus we extract several low-energy bands and reconstruct the low-energy effective Hamiltonian which includes the Coulomb interaction. In fact, we consider the bands within $|E_{k\alpha} - E_F| < 0.1 \text{ Ry}$, in which the extracted bands consist of 4f electrons mainly shown in the figure 1. Furthermore, we approximate the interaction term as band diagonal one, for simplicity. Finally, the low-energy effective Hamiltonian is written as

$$\tilde{H}_{\text{eff}} = \sum_{k,\alpha} E_{k\alpha} a_{k\alpha}^\dagger a_{k\alpha} + U/2 \sum_{k,\alpha \neq \beta} n_{i\alpha} n_{i\beta},$$  \hspace{1cm} (1)$$

where $n_{i\alpha}$ stands for a number operator of a quasi-particle with the site $i$. For the heavy fermion metals, since the Coulomb interaction is strongly renormalized and screened, the amplitude is not so large. In order to calculate the physical quantities, we employ the standard self-consistent
second order perturbation theory with respect to $U$ with local approximation [13, 14]. Thus our treatment may be justified for the weak $U$ region.

3. Results

We divide the 1st Brillouin zone into $80 \times 80 \times 80$ pieces. The tuning parameters are fixed as $J = 7/2$ level $E^f_{7/2} = 0.6$ Ry and hybridization amplitude $V = 0.03$ Ry, respectively, which reproduce the LDA result well. The number of 4f electrons is about 13.35 for the non-interacting case, which agrees with the experimental mean valence.

The figure 1 shows the energy band structure for the non-interacting case. While the analyses by means of the PAM and its extension easily lead to the appearance of a hybridization gap, our model keeps a metallic state and a hybridization gap never appears. It is because the angular dependence of wave-vector $k$ still remains for the matrix element of the hybridization.

With an increase of the Coulomb interaction, the center of gravity of $J = 7/2$ band is shifted to the Fermi level gradually. Although the number of 4f electrons is also reduced due to $U$, the change is not drastic. For example, the number of 4f electrons is about 13.25 for $U = 0.0175$ Ry, which still remains within the experimental value.

Let us discuss the Sommerfeld coefficient and the temperature dependence of $c_v(T)/T$. The former can be obtained from the derivation of the self-energy and the latter is estimated as the numerical difference of the internal energy by temperature. Note that it is difficult to estimate at $T \to 0$, in which $c_v(T)$ has a slightly finite value even at $T \to 0$. Thus we subtract the deviation at $T \to 0$ from $c_v(T)$. With an increase of $U$, the Sommerfeld coefficient also increases, which is shown in Fig.2 inset. In comparison with the experimental result ($\sim 40 \text{ mJ-K}^{-2}\cdot\text{mol}^{-1}$), the appropriate amplitude of $U$ can be estimated as $U = 0.015 - 0.18$ Ry.

Next, the temperature dependence of $c_v(T)/T$ is shown in Fig.2. For the non-interacting case, $c_v(T)/T$ is independent of temperature at very low-temperature region ($T < 0.001$ Ry). With further increase of temperature, $c_v(T)/T$ shows a peak structure. This behavior results from the structure of the Lorentzian-like density of states [12, 13, 14]. Although the peak position is shifted to the lower temperature region with an increase of $U$, the structure remains for any $U$. For example, these appear at $\omega \sim 0.0025$ Ry for $U = 0$ and at $\omega \sim 0.0007$ Ry for $U = 0.015$ Ry. In other words, this peak originates from the band structure of YbAl$_3$.

On the other hand, $c_v(T)/T$ decreases from $T = 0$ with an increase of temperature for the interacting case. As seen in various heavy fermion compounds, the width of $c_v(T)/T$ at $T \sim 0$
becomes narrower because the characteristic energy scale is reduced with an increase of the Coulomb interaction.

For YbAl$_3$, $c_v(T)/T$ decreases monotonically at $T < 30$ K. The peak structure is also observed at $T \sim 70$ K and the amplitude is 80 mJ·K$^{-2}$·mol$^{-1}$ [4, 5, 6]. In the present calculation, for $U \sim 0.015 - 0.0175$ Ry, the peak structure is located at $T \sim 0.0002 - 0.0007$ Ry, which roughly corresponds to 30 – 90 K. The Sommerfeld coefficient corresponds to 20 – 30 mJ·K$^{-2}$·mol$^{-1}$ and $c_v(T)/T$ decreases from $T = 0$. Thus, although there are some disagreements, our obtained $c_v(T)/T$ reproduces well the shape and value of the observed results.

4. Summary

We have discussed quantitatively the Sommerfeld coefficient and temperature dependence of $c_v(T)/T$ of typical heavy fermion YbAl$_3$ by means of the recently proposed effective Hamiltonian with the realistic band structure. The band term of the Hamiltonian consists of the conduction band described by NFE, the localized 4f electrons and the hybridization between these electrons which still keeps the angular dependence of $k$. Furthermore, we have reconstructed the low-energy effective Hamiltonian which consists of the several bands near the Fermi level and the Coulomb interaction.

The temperature dependence of $c_v(T)/T$ is calculated, in which $c_v(T)/T$ decreases from $T = 0$ with an increase of temperature and the peak structure appears at higher temperature for any $U$. For the case of $U \sim 0.015 - 0.0175$ Ry, the obtained $c_v(T)/T$ and the Sommerfeld coefficient reproduces roughly the experimental results. Our proposed effective Hamiltonian may succeed in capturing the quantitative properties of the realistic heavy fermion materials with the conduction band composed of s- or p- electrons.