Mass Enhancement in an Intermediate-Valent Regime of Heavy-Fermion Systems

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We study the mechanism of the mass enhancement in an intermediate-valent regime of heavy-fermion materials. We find that the crossovers between the Kondo, intermediate valent, and almost empty $f$-electron regimes become sharp with the Coulomb interaction between the conduction and $f$ electrons. In the intermediate-valent regime, we find a substantial mass enhancement, which is not expected in previous theories. Our theory may be relevant to the observed nonmonotonic variation in the effective mass under pressure in CeCu$_2$Si$_2$ and the mass enhancement in the intermediate-valent compounds $\alpha$-YbAlB$_4$ and $\beta$-YbAlB$_4$.

KEYWORDS: mass enhancement, Gutzwiller approximation, extended periodic Anderson model, valence fluctuations, heavy-fermion superconductivity, valence transition

The heavy-fermion phenomenon is one of the most remarkable consequences of a strong electron correlation. In some heavy-fermion materials, the effective mass of electrons becomes a thousand times as large as the free-electron mass. Such heavy electron mass is due to the renormalization effect on the hybridization band by the strong Coulomb interaction $U$ between localized $f$-electrons.

After the discovery of the superconductivity in the heavy-fermion compound CeCu$_2$Si$_2$\textsuperscript{1,2} several heavy-fermion superconductors have been investigated. Since the onsite Coulomb interaction is strong in a heavy-fermion system, superconductivity is expected to be unconventional, i.e., other than the $s$-wave, and has been one of the central issues in the research field of solid state physics. In many cases, superconductivity takes place around a magnetic quantum critical point, where the magnetic transition temperature becomes absolute zero. Thus, the superconducting pairing interaction is supposed to be mediated by magnetic fluctuations in these systems.

However, in CeCu$_2$Si$_2$\textsuperscript{2,3} and CeCu$_2$Ge$_2$\textsuperscript{3} superconducting transition temperatures become maximum in high-pressure regions far away from the magnetic quantum critical points. In addition, the superconducting region splits into two regions in CeCu$_2$Si$_{1.5}$Ge$_{0.5}$\textsuperscript{4,5} Thus, the superconductivity in the high-pressure region in these compounds is difficult to be understood by the magnetic fluctuation scenario, and the superconductivity mediated by valence fluctuations is proposed.\textsuperscript{5,6} In these compounds, the effective mass, deduced from specific heat measurements or the temperature dependence of electrical resistivity, decreases rapidly at approximately the pressure where the superconducting transition temperature becomes maximum.\textsuperscript{7,8} The effective mass $m^*$ in heavy-electron systems is closely related to the valence of $f$ ions:\textsuperscript{9,10}

$$m^* = \frac{1 - n_f/2}{1 - n_f}$$ \hspace{1cm} (1)

where $m$ is the free-electron mass and $n_f$ is the number of $f$ electrons per site. This relation is derived for the periodic Anderson model (PAM) with $U \rightarrow \infty$ by the Gutzwiller method. Thus, $m^*$ decreases as $n_f$ decreases. In Ce compounds, $n_f$ decreases under pressure, since the $f$-electron level $\epsilon_f$ in a positively charged Ce ion surrounded by negatively charged ions becomes higher and also the hybridization matrix element $V$ increases. Therefore, we expect that a sharp change in $n_f$ or large valence fluctuations play important roles in the superconductivity in these materials.

However, eq. (1) is derived for the ordinary PAM, which does not show a sharp valence change. Moreover, the effective mass has a peak in CeCu$_2$Si$_2$ under pressure before the superconducting transition temperature becomes maximum.\textsuperscript{9} Such a nonmonotonic variation in the effective mass cannot be expected from eq. (1). Note also that, in CeCu$_2$Ge$_2$, the effective mass shows a shoulder structure before superconducting transition temperature becomes maximum.\textsuperscript{7} This shoulder structure may also become a peak if we can subtract the contributions of magnetic fluctuations, which are large in the low-pressure region. These peak structures may be explained by a combined effect of valence fluctuations and the renormalization described by eq. (1),\textsuperscript{8} but the applicability of eq. (1) to a model with large valence fluctuations is not justified. Thus, we should extend eq. (1) to a model that shows a sharp valence change to understand the superconductivity in CeCu$_2$Si$_2$ and CeCu$_2$Ge$_2$ coherently by the valence fluctuation scenario.

Another important recent issue on the heavy-fermion phenomenon is the heavy-fermion behavior in the intermediate-valent compounds $\alpha$-YbAlB$_4$ and $\beta$-YbAlB$_4$.\textsuperscript{11} $\beta$-YbAlB$_4$ is reported to show superconductivity at a very low temperature.\textsuperscript{12} Although both compounds show heavy-fermion behavior, the valences of Yb ions are +2.73 for $\alpha$-YbAlB$_4$ and +2.75 for $\beta$-YbAlB$_4$.\textsuperscript{13} Thus, the hole numbers in the $f$ level are $n_f = 0.73$ and 0.75 for $\alpha$-YbAlB$_4$ and $\beta$-YbAlB$_4$, respectively. With such $n_f \ll 1$, heavy-fermion behavior is not expected from eq. (1).

In this research, we study an extended periodic Anderson model (EPAM) with the Coulomb interaction $U_{cf}$ between the conduction and $f$ electrons, which induces valence transitions, by the Gutzwiller method. We extend the Gutzwiller method for the PAM developed by Fazekas and Brandow\textsuperscript{10} to the present model. This extension is straightforward but the formulation is lengthy, and here we show only the obtained results. The details of the derivation will be reported elsewhere. Although the EPAM has been investigated by some numerical methods in recent years,\textsuperscript{14-16} the effect of $U_{cf}$ on the mass
The EPAM is given by
\[ H = \sum_{k \sigma} \varepsilon_k c_{k\sigma}^\dagger c_{k\sigma} + \epsilon f \sum_{i} n_{fi\sigma} - V \sum_{k} \langle f_{k\sigma}^\dagger c_{k\sigma} + \text{h.c.} \rangle + U \sum_{i} n_{fi\sigma} n_{fi\bar{\sigma}} + U_{cf} \sum_{i\sigma} n_{ci\sigma} n_{fi\sigma}, \]

where \( c_{k\sigma} \) and \( f_{k\sigma} \) are the annihilation operators of the conduction and \( f \) electrons, respectively, with the momentum \( k \) and the spin \( \sigma \). \( n_{ci\sigma} \) and \( n_{fi\sigma} \) are the number operators at site \( i \) with \( \sigma \) of the conduction and \( f \) electrons, respectively. \( \varepsilon_k \) is the kinetic energy of the conduction electron. In the following, we set the energy level of the conduction band as the origin of energy, i.e., \( \sum \varepsilon_k = 0 \). We set \( U \rightarrow \infty \), since the Coulomb interaction between well-localized \( f \) electrons is large.

We consider the variational wave function given by \( |\psi\rangle = P_{ff} P_{cf} |\phi\rangle \), where \( P_{ff} = \prod_{i} [1 - \epsilon n_{fi\sigma}] \) excludes the double occupancy of \( f \) electrons at the same site, and \( P_{cf} = \prod_{i\sigma} [1 - (1 - \epsilon) n_{ci\sigma} n_{fi\sigma}] \) is introduced to deal with the on-site correlation between conduction and \( f \) electrons. \( \epsilon \) is a variational parameter. The one-electron part of the wave function is given by \( |\phi\rangle = \prod_{k} c_{k\sigma}^\dagger c_{k\bar{\sigma}} + a(k) f_{k\sigma}^\dagger f_{k\bar{\sigma}} \) [1], where \( k \) is the Fermi momentum, \( |0\rangle \) denotes vacuum, and \( a(k) \) is determined variationally. Here, we have assumed that the number of electrons \( n \) per site is smaller than 2.

Then, we apply Gutzwiller approximation. Here, we introduce the quantity \( d_{ci\sigma} = \sum_{\sigma} (n_{ci\sigma}(n_{fi\sigma} + n_{fi\sigma})) / L \), where \( \langle \cdots \rangle \) denotes the expectation value and \( L \) is the number of lattice sites. In evaluating expectation values by Gutzwiller approximation, we determine \( d_{ci\sigma} \), which has the largest weight in summations. The result is \( g^2 = [d_{ci\sigma}(1 - n_{ci\sigma} + d_{ci\sigma})]/[(n_{ci\sigma} - d_{ci\sigma}) n_{ci\bar{\sigma}}] \), where \( n_{ci\sigma} = \sum_{\sigma} (n_{ci\sigma}/L) \), and \( n_{fi\sigma} = \sum_{\sigma} (n_{fi\sigma}/L) \). This is the same form as that in the Hubbard model, if we regard \( n_{ci\sigma} \) as \( n_{i\sigma}^H \), \( n_{ci\bar{\sigma}} \) as \( n_{i\bar{\sigma}}^H \), and \( d_{ci\sigma} \) as \( d^H \), where \( n_{i\sigma}^H \) and \( d^H \) are the numbers of \( \sigma \)-spin electrons and doubly occupied sites per lattice site, respectively, in the Hubbard model, and \( \sigma \) denotes the opposite spin of \( \sigma \).

In the following, we assume a paramagnetic state, i.e., \( n_{ci\sigma} = n_{i\sigma}/2 \), and \( n_{ci\bar{\sigma}} = n_{i\bar{\sigma}}/2 = (n - n_{i\sigma})/2 \), and \( d_{ci\sigma} = d/2 \), and optimize the wave function so that it has the lowest energy. In the following, we regard \( d \) as a variational parameter instead of \( g \) as is done in ordinary Gutzwiller approximation. Then we find that \( a(k) = 2 \tilde{V}_1 / (\tilde{\varepsilon}_f - \tilde{\varepsilon}_k + [\tilde{\varepsilon}_f - \tilde{\varepsilon}_k^2 + 4 \tilde{V}_2]^1/2) \), where \( \tilde{V}_2 = \sqrt{V_2} / (\sqrt{\varepsilon} \times q \times V) \) and \( \tilde{\varepsilon}_k = q \varepsilon_k \). \( \tilde{\varepsilon}_k \) is the renormalized \( f \)-level obtained by solving integral equations, as we will show later. The renormalization factors are given by \( g = [n_{i\sigma}^2 - d(1 - n_{i\sigma}/2)(1 - n_{i\sigma}/2 + d/2)]/[n_{i\sigma}^2 - (1 - n_{i\sigma}/2)(1 - n_{i\sigma}/2 + 2d/2)]^{1/2} \), \( q_{ci\sigma} = [n_{ci\sigma} - d_{ci\sigma}(1 - n_{ci\sigma} + d_{ci\sigma})]^{1/2} + [d_{ci\sigma}(n_{ci\sigma} - d_{ci\sigma})]^{1/2} / [n_{ci\sigma} - (1 - n_{ci\sigma})] \), and \( q_{c\bar{i}i\sigma} = [n_{ci\bar{\sigma}} - d_{ci\bar{\sigma}}(1 - n_{ci\bar{\sigma}} + d_{ci\bar{\sigma}})]^{1/2} + [d_{ci\bar{\sigma}}(n_{ci\bar{\sigma}} - d_{ci\bar{\sigma}})]^{1/2} / [n_{ci\bar{\sigma}} - (1 - n_{ci\bar{\sigma}})] \). \( q_{c\bar{i}i\sigma} \) has the same form as the renormalization factor of quantum fluctuations in the Hubbard model, if we consider \( n_{i\sigma} \) as a functional of \( \phi \) and \( a(k) \), the mass enhancement factor becomes large as \( n_{i\sigma} \rightarrow 1 \), which is consistent with the previous result on the PAM. Third, we consider a case with an intermediate \( \epsilon \) with a large magnitude. In this case, \( n_{i\sigma} \rightarrow 1 \) and \( n_{i\bar{\sigma}} \rightarrow n - 1 \). The energy is approximately given by the sum of \( L[\epsilon_f + (n_{i\sigma} - 1) U_{cf} + \text{the energy of the free conduction band with } n_{i\sigma} = n - 1] \). We call this regime the intermediate-valent regime. In this intermediate-valent regime, the mass enhancement factor becomes large as \( n_{i\sigma} + n_{i\bar{\sigma}} \rightarrow 1 \) and \( d \rightarrow 0 \). This mass enhancement in the intermediate-valent regime is not realized in the ordinary PAM and is a result of the effect of \( U_{cf} \). In the following, we consider a simple model of the kinetic energy: the density of states per spin is given by \( \rho(\epsilon) = 1/(2W) \) for \( -W \leq \epsilon \leq W \); otherwise, \( \rho(\epsilon) = 0 \).

Now, we show our calculated results. Figure 1(a) shows \( n_{i\sigma} \) as a function of \( \epsilon_f \) for several values of \( U_{cf} \) for \( V/W = 0.1 \) and \( n = 1.25 \). For a large \( U_{cf} \), we recognize the three regimes mentioned above. A first-order phase transition occurs from the intermediate-valent regime to the \( n_{i\sigma} \rightarrow 0 \) regime for \( U_{cf}/W > 1.24 \). We observe hysteresis by increasing and decreasing \( \epsilon_f \) across the first-order phase transition point, and here we show the values of the state that has the lower energy. Figure 1(b) shows the valence susceptibility \( \chi_V = -d \epsilon_f / d \epsilon_f \) as a function of \( \epsilon_f \). The valence susceptibility enhances around the boundaries of three regimes for a large \( U_{cf} \). For a small \( U_{cf} \), such a boundary is not clear and \( \chi_V \) has a broad peak. Figure 1(c) shows the mass enhancement factor \( 1/\Delta n(k_f) \) as a function of \( \epsilon_f \). In addition to the enhancement for \( n_{i\sigma} \rightarrow 1 \) in the ordinary PAM, we find another region, that is, the intermediate-valent regime \( n_{i\sigma} \approx 2 - n \), in which the mass enhancement factor becomes large. This enhancement, particularly as a peak as a function of \( \epsilon_f \), is not expected for the PAM without \( U_{cf} \). The large effective mass in the intermediate-valent compounds \( \alpha\text{-YbAlB}_4 \) and \( \beta\text{-YbAlB}_4 \).
and the nonmonotonic variation in the effective mass under pressure in CeCu$_2$Si$_2$ may be explained by the present theory.

To clearly observe the effect of $U_{cf}$ on the mass enhancement, we show $1/\Delta m(k_F)$ as a function of $n_f$ in Fig. 2. The thin line, which is almost overlapping with the $U_{cf} = 0$ data, represents the mass enhancement factor $(1 - n_f/2)/(1 - n_f)$ obtained for the PAM with $U_{cf} = 0$ and $g = 1$. By increasing $U_{cf}$, $1/\Delta m(k_F)$ becomes large, particularly in the intermediate-valent regime $n_f \approx 2 - n$.

In Fig. 3, we show the valence susceptibility $\chi_V$ as a function of $\epsilon_f$ and $U_{cf}$ for $n = 1.25$, 1.50, and 1.75. In this figure, we also draw the first-order valence transition lines and their critical points. The crossover lines, represented by the dotted lines, are determined by comparing the energies of the three extreme states: $n_f = 0$, $n_f = 1$, and $n_f + n_i/2 = 1$ with $d = 0$. The region where $\chi_V$ becomes large is captured well by the crossover lines obtained by such a simple consideration. For $n = 1.25$, the first-order valence transition occurs only from the intermediate-valent regime to $n_f = 0$ regime, while for $n = 1.75$ it occurs only between the Kondo and intermediate-valent regimes, within the $U_{cf}$ range presented here. $n_f$ in the intermediate-valent regime differs between these two cases: $n_f \approx 0.75$ for $n = 1.25$ and $n_f \approx 0.25$ for $n = 1.75$. The first-order transition seems to occur easily between very different states, that is, a crossover accompanying a large valence change tends to become a first-order phase transition. Between these two cases, for $n = 1.50$, both the transitions take place for $U_{cf}/W > 2.88$. Note that, since only the $n = 1.75$ case is well investigated in previous studies, the first-order transition between the intermediate valent and $n_f = 0$ regimes has not been elucidated.
In summary, we have studied the extended periodic Anderson model with $U_{cf}$ by Gutzwiller approximation. We have found that there are three regimes, that is, the $n_f = 0$, intermediate valent, and Kondo regimes, are clearly defined for a large $U_{cf}$. Then, we have found that, in the intermediate-valent regime, the effective mass is enhanced substantially. According to the present theory, the large mass enhancement in the intermediate-valent regime indicates a large $U_{cf}$. Thus, our theory provides helpful information for searching a superconductor with valence-fluctuation-mediated pairing.

Figure 4 shows the mass enhancement factor $1/\Delta n(k_F)$ as a function of $\epsilon_f$ and $U_{cf}$ for $V/W = 0.1$ for (a) $n = 1.25$, (b) $n = 1.50$, and (c) $n = 1.75$. The lines and circles are the same as those in Fig. 3.

Figure 4 (Color online) $1/\Delta n(k_F)$ as a function of $\epsilon_f$ and $U_{cf}$ with $V/W = 0.1$ for (a) $n = 1.25$, (b) $n = 1.50$, and (c) $n = 1.75$. The lines and circles are the same as those in Fig. 3.

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