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Temperature Dependence of Thermopower in Strongly Correlated Multiorbital Systems

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Temperature dependence of thermopower in the multiorbital Hubbard model is studied by using the dynamical mean-field theory with the non-crossing approximation impurity solver. It is found that the Coulomb interaction, the Hund coupling, and the crystal filed splitting bring about non-monotonic temperature dependence of the thermopower, including its sign reversal. The implication of our theoretical results to some materials is discussed.

KEYWORDS: thermopower, Hubbard model, multi-orbital system

The thermopower in strongly correlated electron systems has been attracting much attention [1–13]. The thermopower is the entropy flow by the electric current, so that the spin and orbital degrees of freedom are of importance to enhance the thermopower [1,6,8,10]. In the strongly correlated systems, the thermopower often shows the non-monotonic temperature dependence [9,12,13]. Furthermore, in the multiorbital correlated system, the electronic state reflects the crystal field splitting and the Hund coupling. So far, the thermopower in the multiorbital correlated electron system has been studied by several groups [8,9], while the effect of the crystal field splitting and the Hund coupling has not been fully examined on the temperature dependence of the thermopower in multiorbital correlated systems.

In this paper, we study the thermopower in the multiorbital Hubbard model given by,

$$\begin{aligned} H &= \sum_{k,m,\sigma} (\varepsilon_k + \Delta_m)\, c^\dagger_{km\sigma} c_{km\sigma} + U \sum_{i,m} n_{im\uparrow} n_{im\downarrow} \\ &+ U' \sum_{i,m<m',\sigma,\sigma'} n_{im\sigma} n_{im'\sigma'} \\ &- J \sum_{i,m<m',\sigma,\sigma'} \left(c^\dagger_{im\sigma} c_{im\sigma'} c^\dagger_{im'\sigma'} c_{im'\sigma} + \text{h.c.} \right) \\ &+ I \sum_{i,m<m'} \left(c^\dagger_{im\uparrow} c^\dagger_{im\downarrow} c_{im'\downarrow} c_{im'\uparrow} + \text{h.c.} \right), \end{aligned} \tag{1}$$

with the electron spin $\sigma(=\uparrow,\downarrow)$, the orbital index m, and the dispersion relation of the non-interacting electrons ε_k. Here, Δ_m denotes the energy level of the m-th orbital, U (U') is the intraorbital (interorbital) Coulomb repulsion, J and I are the magnitude of Hund coupling and pair hopping, respectively.

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Below, we impose the conditions, $U = U' + J + I$ and $J = I$ assuming the orbital symmetry, t_{2g} or e_g.

The many-body interactions are dealt with using the dynamical mean-field theory (DMFT) [2, 3, 5, 7, 9, 12–14] with the non-crossing approximation (NCA) [2, 15, 16] impurity solver. In this work, we consider the semicircular density of states for the non-interacting system,

$$D_0(\omega) = \frac{2}{\pi W_0^2}\sqrt{W_0^2 - \omega^2}. \tag{2}$$

The thermopower Q is then given by $Q = -(k_{\rm B}/e)(A_1/A_0)$ with,

$$A_l = \frac{\pi}{\hbar k_{\rm B}} \sum_{m,\sigma} \int d\omega d\epsilon \frac{(\beta\omega)^l}{4\cosh^2(\beta\omega/2)} \left[\rho_{m,\sigma}(\omega,\epsilon)\right]^2 D_0(\epsilon), \tag{3}$$

where $\beta = 1/k_{\rm B}T$ [3,5] . The spectral density $\rho_{m,\sigma}(\omega,\epsilon)$ is given by $\rho_{m,\sigma}(\omega,\epsilon) \equiv -{\rm Im}G_{m,\sigma}(\omega,\epsilon)/\pi$ with the Green's function $G_{m,\sigma}(\omega,\epsilon)$ obtained by DMFT. Below, W_0 is taken to be unity.

First, we examine the two-orbital system with $\Delta_1 = -\Delta_2 = -\Delta/2$. Figures 1 (a) and (b) show the effect of crystal-field splitting Δ and J on the temperature dependence of Q, respectively [17]. As in the single-orbital model [13], we find the non-monotonic temperature dependence of the ther-

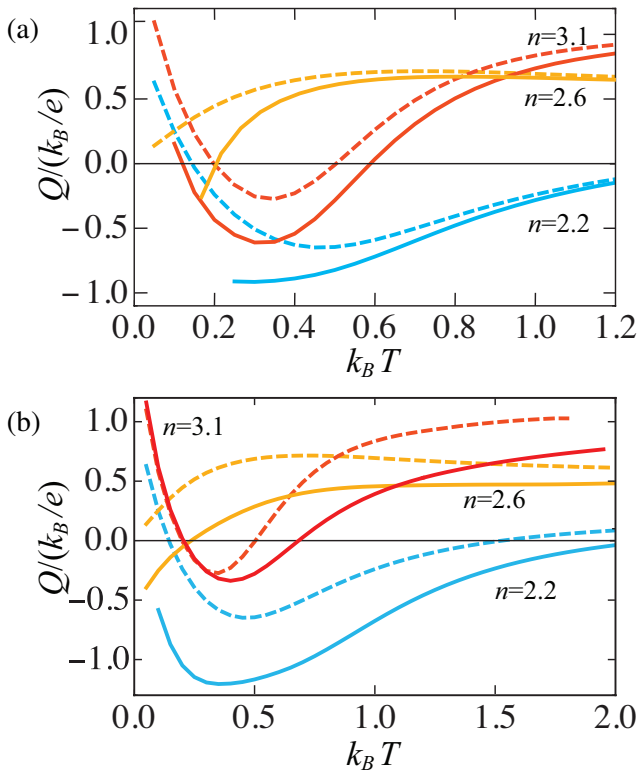

Fig. 1. (Color online) (a) Temperature dependence of the thermopower for $U = 3$ and $J = 0$ with n=2.2, 2.6, and 3.1. The broken (solid) line indicates the thermopower for $\Delta = 0$ ($\Delta = 0.4$). (b) Temperature dependence of the thermopower for $U = 3$, and $\Delta = 0$ with n=2.2, 2.6, and 3.1. The broken (solid) line represents the thermopower for $J = 0$ ($J = 0.5$).

mopower due to the Coulomb interaction. This behavior resembles the experimental report on doped

vanadates [12]. By introducing finite Δ and/or J, all the lines are shifted down (see the broken and solid lines in Fig. 1).

Here, we briefly summarize the Heikes formula [1, 6, 8, 10] being useful to understand the non-monotonic temperature dependence and the shifts by Δ and/or J. The following two cases are considered in the high-temperature limit; (1) $Q_1 = Q(T \to \infty, U)$ by keeping $k_{\rm B}T < U$, and (2) $Q_2 = Q(T \to \infty, U)$ by keeping $k_{\rm B}T > U$. In the case (1), $U \to \infty$ is taken before $T \to \infty$. In this limit, except for integer fillings, one needs to consider two kinds of sites, A and B, where the electron occupancy in A-site, $n_{\rm A}$, differs from that in B-site, $n_{\rm B}$, by one, i.e., $n_{\rm A} - n_{\rm B} = 1$. The each sites have the local degeneracies, $g_{\rm A}$ and $g_{\rm B}$, in accordance with the electron occupancy. Therefore, the high-temperature limit Q_1 is given by,

$$Q_1 = -\frac{k_{\rm B}}{e} \ln \frac{g_{\rm A}}{g_{\rm B}} - \frac{k_{\rm B}}{e} \ln \left(\frac{n - n_{\rm A}}{n_{\rm B} - n} \right), \tag{4}$$

where n is the electron density with $n_{\rm A} > n > n_{\rm B}$. In the case (2), on the other hand, U is of less importance, so that Q_2 in the ν-orbital system is given by,

$$Q_2 = -\frac{k_{\rm B}}{e} \ln \left(\frac{2\nu - n}{n} \right). \tag{5}$$

Note that 2 in Eq. (5) is associated with the spin degree of freedom.

The non-monotonic temperature dependences shown in Fig. 1 are understood by the change from Q_1 to Q_2. As an example, let us consider the temperature dependence of Q for $n = 3.1$ with $U = 3$, $J = I = 0$ and $\Delta = 0$ in Fig. 1(a) (see the red broken line). In this case, $(n_{\rm A}, n_{\rm B}) = (4, 3)$ and $g_{\rm A}/g_{\rm B} = 1/4$ result in negative Q_1, while Q_2 is positive. For the temperature region $k_{\rm B}T < U$, the Coulomb interaction is in effect for the entropy transport, and hence, Q approaches Q_1 [1, 6, 8, 10, 12, 13]. On the other hand, at high-temperatures $k_{\rm B}T \gg U$, the effect of U is of less importance, so that Q approaches Q_2. The change from Q_1 to Q_2 is seen in the temperature dependence of Q in Fig. 1(a), i.e., the broken line for $n = 3.1$ changes the sign from negative to positive at the temperature region, $0.3 < k_{\rm B}T$. This picture consistently explains the other cases shown by broken lines in Fig. 1.

By including Δ, Q is shifted down in the negative direction as shown in Fig. 1(a) (see the difference between the broken and solid lines). For finite Δ, electrons prefer to go into the lower-energy-level orbital. Let us consider the effect of Δ in the formula Q_1. It is noted that the first term of Q_1, i.e., $-(k_{\rm B}/e)\ln(g_{\rm A}/g_{\rm B})$ decreases for $\Delta \to \infty$ in all the cases in Fig. 1(a). (For example, for $2 < n < 3$, $g_{\rm A}/g_{\rm B} = 4/6$ for $\Delta = 0$, while $g_{\rm A}/g_{\rm B} = 2/1$ for $\Delta \to \infty$.) Hence, Q_1 is shifted down in the negative direction.

Next, we discuss the effect of Hund coupling on the thermopower based on Q_1 (see Fig. 1(b)). Note that the condition $U' - J = U - 3J$ (=3) is imposed to roughly fix the Mott gap. Consequently, the magnitude of the on-site Coulomb interaction U increases by including a finite J. Therefore, the temperature region where the Coulomb interaction is in effect on Q is expanded, and hence the lines in Fig. 1(b) are shifted down in the high temperature region [13]. In addition to the shift by U, the lines for $n = 2.2$ and $n = 2.6$ in Fig. 1(b) are shifted down particularly around $k_{\rm B}T \sim 0.5$. The shifts are explained by the change of spin degeneracy by J. For $n = 2.2$ and $n = 2.6$, i.e., $2 < n < 3$ with Δ=0, $g_{\rm A}/g_{\rm B} = 4/6$ for J=0, while $g_{\rm A}/g_{\rm B} = 4/3$ for $J \to \infty$. This leads to the change in Q_1 and then the shifts of the lines for $n = 2.2$ and $n = 2.6$ in Fig. 1(b) around $k_{\rm B}T \sim 0.5$. For $3 < n < 4$, on the other hand, the degeneracies $g_{\rm A}$ and $g_{\rm B}$ are not modified by J. Consequently, the result for $n = 3.1$ around $k_{\rm B}T \sim 0.5$ is not much affected by J in comparison with the other electron densities at $2 < n < 3$. The consideration on Q_1 and Q_2 consistently explains the effects of J on the calculated results shown in Fig. 1(b).

As a summary of the two-orbital model, the discussion on Q_1 and Q_2 gives the following understanding for the temperature dependence of thermopower: (i) The strong Coulomb interaction gives

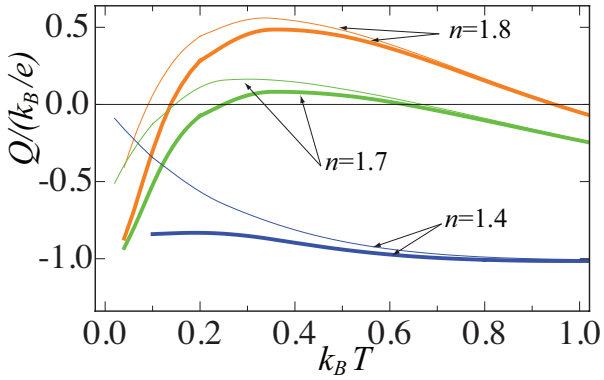

Fig. 2. (Color online) Temperature dependence of the thermopower in the three-orbital Hubbard model for $U' - J = 3$ and $J = 0.5$ with n=1.4, 1.7, and 1.8. The thin and thick lines are for $\Delta = 0$ and $\Delta = 0.25$, respectively.

the non-monotonic temperature dependence, i.e., the change from Q_1 to Q_2. (ii) The effect of crystal field splitting and Hund coupling is explained by the first term of Q_1.

Finally, we consider the three-orbital model with $\Delta_1 = \Delta_2 = -\Delta_3 = \Delta$, and the electron densities $1 < n < 2$. Figure 2 shows the temperature dependence of Q in the three-orbital model for n=1.4, 1.7, and 1.8 [17]. Here, we take the parameter set, $U' - J = 3$ and $J = 0.5$. The consideration on Q_1 and Q_2 is again useful to understand the non-monotonic temperature dependence and the effect of Δ. For example, for $n = 1.8$ with $\Delta = 0$, $(n_{\rm A}, n_{\rm B}) = (2, 1)$ and $g_{\rm A}/g_{\rm B} = 9/6$, and therefore Q_1 is positive, while Q_2 is negative. This explains the temperature dependence of Q for this doping. By introducing Δ, the first term of Q_1, $-(k_{\rm B}/e)\ln(g_{\rm A}/g_{\rm B})$, "decreases" in all the cases in Fig. 2 because $g_{\rm A}/g_{\rm B}$ is increased to $6/2$ as $\Delta \to \infty$. Hence, all the lines shown in Fig. 2 are shifted down in the negative direction.

In our previous study [12], we have reported the non-monotonic temperature dependence of the thermopower in $La_{1-x}Sr_xVO_3$, which is well explained by considering Q_1 and Q_2 in the three orbital system. In this material, the vanadium valence is in between +3 (d^2) and +4 (d^1) and the transport properties are determined by the t_{2g} manifold associated with the three orbital system. In this study, we have clarified the effect of Δ and J on the temperature dependence of the thermopower. In reality, the crystal field splitting can be modified by applying a pressure. Thus, high pressure measurements are highly desired to test our theoretical results.

We have shown the temperature dependences of the thermopower in the two- and three-orbital Hubbard models by using the dynamical mean-field theory with the non-crossing approximation impurity solver. It has been clarified how the Hund coupling, the crystal field splitting and the Coulomb interaction produce the non-monotonic temperature behavior of the thermopower. It is also found that the sign of thermopower is changed by temperature and electron density. The entropy consideration at high temperatures, i.e., Heikes formula, consistently explains the effect of the crystal field splitting and the Hund coupling on the thermopower.

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