Effects of Spin and Orbital Degeneracy on the Thermopower of Strongly Correlated Systems

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We study thermopower in strongly correlated electron systems with orbital degeneracy using numerical diagonalization method on finite-size clusters. It is shown that the thermopower is strongly enhanced by the spin and orbital degrees of freedom, but the resistivity is significantly less affected. A key for the strategy of new thermoelectric materials in transition metal oxides is proposed in the light of the theory.

Thermoelectric materials have attracted much attention recently. They generate electric energy from heat using thermoelectric effect of solids. Since the generation of electric energy is not accompanied with pollution essentially, the thermoelectric materials are available for waste heat utilization, power source of deep-space probes, and so on.

So far, semiconductors have mostly been used for thermoelectric materials. In application, not only large thermopower but also low electrical resistivity is required. However, the thermopower and the resistivity are not independent of each other, but depend on carrier density. Although the thermopower increases logarithmically with decreasing carriers, the resistivity is also enhanced. Consequently, the optimum carrier density is estimated to be 10^{18}–10^{19} cm^{-3}. Under this restriction, the present thermoelectric materials have been synthesized [1].

Recently, Terasaki *et al.* [2] have shown the large thermopower in the layered compound $NaCo_2O_4$. The thermopower of this oxide increases with increasing temperature, and reaches 100 μV/K at 300 K. The temperature dependence of the in-plane resistivity shows metallic behavior and the resistivity at 300 K is 200 $\mu\Omega$ cm. The estimated carrier concentration is of the order of 10^{22} cm^{-3} which is comparable with a typical value for metals and different from that in the conventional thermoelectric materials. The oxide is a typical strongly correlated electron system [2,3], and the transport properties are not well understood.

Theoretical study of thermopower in strongly correlated electron systems has been developed by several authors [4–11] based on the Hubbard model. At high temperatures, the thermopower is obtained from the entropy consideration. This is known as the Heikes formula [12]. Within the framework, the importance of the spin [4,6] and orbital degrees of freedom [7,8] have been discussed. There exist several attempts to study the temperature dependence of thermopower using retraceable path approximation [5] and dynamical mean-field theory [9,10]. Jaklič and Prelovšek [11] examined the temperature dependence of the chemical potential using finite-temperature Lanczos method and gave a qualitative discussion of the thermopower in cuprates. Because the thermopower must obey the Heikes formula at high temperatures, there is no simple way to extend the theory to the finite-temperature

region. In the multiband systems, the atomic parameters, such as Hund's-rule coupling and energy-level splitting between orbitals, affect the electronic structure, so that the study of spin and orbital degrees of freedom on thermopower is complicated.

In this Letter, we will show that spin and orbital degrees of freedom cause large thermopower in contrast with the resistivity in strongly correlated electron systems. We adopt the numerical diagonalization method on finite-size clusters and examine the temperature dependence of thermopower and resistivity. The origin of the large thermopower in $NaCo_2O_4$ and the important ingredients for the strategies of new thermoelectric materials are proposed in the light of our theory.

First, we apply the numerical diagonalization method to the one-dimensional *t-J* model. The Hamiltonian is written as

$$H = -t \sum_{i\sigma}(c_{i,\sigma}^{\dagger} c_{i+1,\sigma} + c_{i+1,\sigma}^{\dagger} c_{i,\sigma}) + J \sum_{i} \vec{S}_i \cdot \vec{S}_{i+1}, \quad (1)$$

where t is the transfer integral of an electron between neighboring sites, $c_{i,\sigma}^{\dagger}$ and $c_{i+1,\sigma}$ are creation and annihilation operators of electron with spin σ ($= \uparrow, \downarrow$) at sites i and $i + 1$, respectively, and J is the antiferromagnetic superexchange interaction between neighboring spins. The doubly occupied state in a site is excluded. The thermopower is given by

$$Q = -\frac{1}{eT}\frac{M_{12}}{M_{11}} + \frac{\mu}{eT}, \quad (2)$$

where e is the absolute value of electron charge and μ is the chemical potential. M_{1l} ($l = 1, 2$) is expressed as

$$M_{1l} = \int_0^{\infty} dt \int_0^{1/k_B T} d\tau$$
$$\times \text{Tr}[e^{-H/k_B T} j_{1,q=0}(-t - i\tau) j_{l,q=0}], \quad (3)$$

where the symbol "Tr" denotes trace and is the summation over some complete set of states, and j's are particle current ($l = 1$) and energy flux operators ($l = 2$) in the Heisenberg representation, respectively. These operators are obtained from the following procedure. The conservation law of the particle density and energy density gives

the expression of current and energy flux operators in real space. The particle density and energy density at site r are defined as

$$n_r = \sum_\sigma c^\dagger_{r,\sigma} c_{r,\sigma}, \tag{4}$$

$$h_r = -\frac{t}{2} \sum_{\delta=\pm 1,\sigma} (c^\dagger_{r,\sigma} c_{r+\delta,\sigma} + \text{H.c.})$$
$$+ \frac{J}{2} \sum_{\delta=\pm 1} \vec{S}_r \cdot \vec{S}_{r+\delta}, \tag{5}$$

respectively. The conservation law is expressed by the following equations:

$$-i[n_r, H] = \sum_{r,\delta} \delta^{-1} j_{1,(r,r+\delta)}, \tag{6}$$

$$-i[h_r, H] = \sum_{r,\delta} \delta^{-1} j_{2,(r,r+\delta)}, \tag{7}$$

where $\sum_{\delta>0} j_{1,(r,r+\delta)}$ and $\sum_{\delta>0} j_{2,(r,r+\delta)}$ define the current and energy flux operators in forward direction, respectively. The Fourier transformed operator $j_{l,q}$ is defined as

$$\sum_{\delta>0} j_{1,(r,r+\delta)} = \frac{1}{L} \sum_q j_{l,q} \exp[iqr], \tag{8}$$

where L denotes the number of unit cells. The chemical potential μ is calculated as a function of temperature and number of electrons N using the following equation:

$$N = \frac{\sum_{N_e} \text{Tr}[e^{-(H-\mu N_e)/k_B T} N_e]}{\sum_{N_e} \text{Tr}[e^{-(H-\mu N_e)/k_B T}]}. \tag{9}$$

The summation is performed over all possible number of electrons N_e. We have diagonalized the Hamiltonian (1) on a 12-site periodic chain with 6 holes using Householder method and calculated the thermopower. The result is shown in Fig. 1. With increasing temperature, the absolute value of the thermopower increases rapidly up to $k_B T \sim t$ and saturates at high temperatures. This is consistent with the previous study [5]. The thermopower approaches the value $-(k_B/e)\ln 2$ which is given by the Heikes formula [4,5]. This value is caused by spin degeneracy.
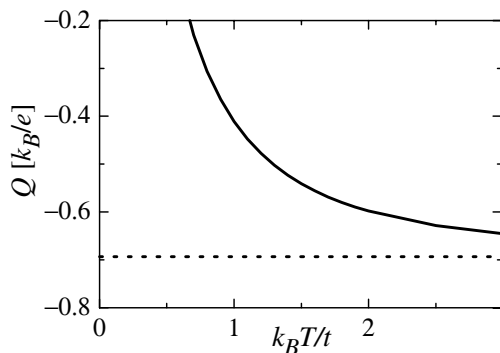

FIG. 1. Thermopower in the one-dimensional t-J model on a 12-site periodic chain with six holes. $J/t = 0.25$ is used. The dotted line indicates $-\ln 2$ which is given by the Heikes formula.

The numerical diagonalization method easily takes account of the atomic parameters such as Hund's-rule coupling and energy-level splitting between orbitals to examine the electronic structure in a finite-size system. Let us examine the effects of spin and orbital degrees of freedom on thermoelectric properties using this method. We examine thermopower and electrical resistivity in the following model:

$$H = -t \sum_{i\nu\sigma} (c^\dagger_{i,\nu,\sigma} c_{i+1,\nu,\sigma} + \text{H.c.}) + J \sum_{i,\nu} \vec{S}_{i\nu} \cdot \vec{S}_{i+1,\nu}$$
$$+ J_H \sum_i \vec{S}_{i,a} \cdot \vec{S}_{i,b} + \sum_{i,\nu} \Delta_\nu n_{i,\nu}, \tag{10}$$

where ν ($= a, b$) is the index of orbitals and J_H is the Hund's-rule coupling. The energy level of orbitals is expressed as Δ_ν. In the following, Δ denotes the energy-level splitting $\Delta_a - \Delta_b$. In this model, the doubly occupied state in an orbital is excluded. The number of electrons N is taken to be larger than the number of unit cells L. We calculate the thermopower and the resistivity ρ ($= L \text{Tr}[\exp(-H/k_B T)]/(e^2 M_{11})$). In Fig. 2, the results are shown for various Δ as functions of temperature in the system with $L = 6$ and $N = 10$. In the calculation, periodic boundary condition is used. The resistivity shows the linear temperature dependence but is almost independent of Δ. On the other hand, the thermopower decreases with increasing Δ and depends on temperature monotonously up to $\Delta \sim k_B T$.

Let us examine these behaviors at high temperatures ($t \ll k_B T$). As shown by Chaikin and Beni [4], the contribution from the first term in the expression of the
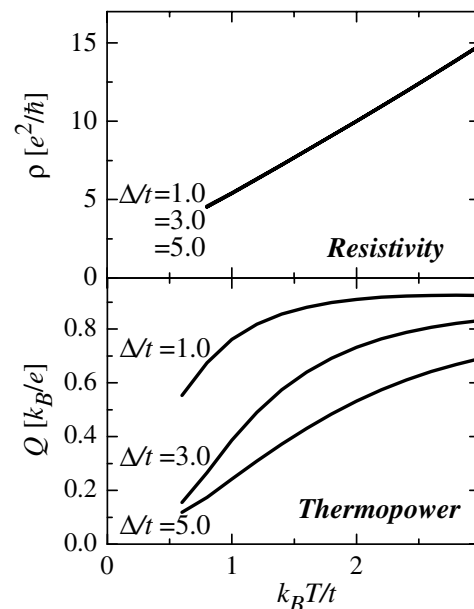

FIG. 2. Thermopower and resistivity in the model given by Eq. (10) with $L = 6$ and $N = 10$ in periodic boundary condition. $J/t = 0.25$ and $J_H/t = -10$ are used.

thermopower Eq. (2) is small at high temperatures. We introduce the entropy s written as $s = k_B \ln g$ where g denotes the degeneracy of high-temperature states. Using the relation between chemical potential and entropy, the thermopower at high temperatures is given by

$$Q = -\frac{k_B}{e} \frac{\partial \ln g}{\partial N} . \quad (11)$$

Our next task is to calculate the degeneracy g. In the model given by Eq. (10), there are two kinds of sites, since each site has two orbitals: one of the orbitals is occupied by an electron and both orbitals are occupied by electrons. We denote the sites as (I) and (II), respectively. Therefore, g is given by the total number of ways of arranging the two kinds of sites and the internal degree of freedom of the sites:

$$g = [g_{(I)}]^{2L-N}[g_{(II)}]^{N-L} \frac{L!}{(N-L)!\,(2L-N)!}, \quad (12)$$

where $g_{(I)}$ and $g_{(II)}$ are the degeneracies of the sites (I) and (II), respectively. Using Stirlings approximation, Eq. (11) is expressed as

$$Q = \frac{k_B}{e}(\ln g_{(I)} - \ln g_{(II)}) - \frac{k_B}{e} \ln\left(\frac{x}{1-x}\right), \quad (13)$$

where $x = 2 - N/L$. The degeneracies $g_{(I)}$ and $g_{(II)}$ originate from spin and orbital degrees of freedom and depend on temperature. First, let us consider the case that $t, \Delta \ll k_B T \ll J_H$. In this case, on site (I), an electron is distributed to both orbitals and $g_{(I)}$ is estimated to be 4 due to the spin and orbital degrees of freedom. On the other hand, on site (II), two electrons form a spin-1 state. Therefore, we obtain $g_{(II)}$ to be 3. As the energy-level splitting Δ increases, an electron on site (I) tends to occupy the stable orbital. In other words, the contribution of the orbital degree of freedom to $g_{(I)}$ decreases with increasing Δ. It is expected that the suppression of $g_{(I)}$ causes the decrease in the thermopower through the first term in Eq. (13). In Fig. 3, the Δ dependence of the thermopower is shown as a function of temperature up to $k_B T/t = 20$. The dotted line indicates the value given by Eq. (13) for $g_{(I)} = 4$, $g_{(II)} = 3$, and $x = 2 - 10/6$. We find that the maximum value of the thermopower is obtained at $k_B T \sim \Delta$ and approaches the dotted line with decreasing Δ. For $k_B T \gtrsim \Delta$, the thermopower decreases with increasing temperature. This behavior is also understood by Eq. (13). In the case that $t, \Delta, J_H \ll k_B T$, the ferromagnetic coupling J_H does not play any role, so that the spin of each electron contributes to the degeneracy $g_{(II)}$ on site (II). As a result, $g_{(II)}$ is 4. The broken line in Fig. 3 shows the value obtained from Eq. (13) for $g_{(I)} = 4$, $g_{(II)} = 4$, and $x = 2 - 10/6$. The numerical results show that the thermopower at high temperatures ($t, \Delta, J_H \ll k_B T$) approaches this value with increasing temperature. Because the high-temperature value of the
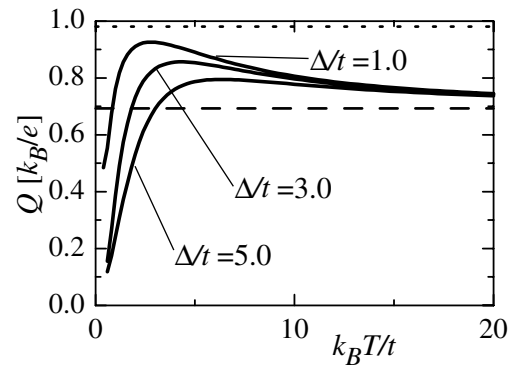

FIG. 3. Thermopower in the model given by Eq. (10). The parameters are the same as those in Fig. 2. The dotted and broken lines are the high-temperature values of thermopower Eq. (13) for $t, \Delta \ll k_B T \ll J_H$ and $t, \Delta, J_H \ll k_B T$, respectively.

thermopower at $t, \Delta, J_H \ll k_B T$ is smaller than that at $t, \Delta \ll k_B T \ll J_H$, the thermopower shows maximum at $k_B T \sim \Delta$.

The effect of spin and orbital degrees of freedom on thermopower is understood as follows. Suppose that the site (II) is on the site i and the site (I) is on the site $i + 1$. Let an electron move from i to $i + 1$. Then, the sites i and $i + 1$ become (I) and (II), respectively. In the process, the charge $-e$ moves from i to $i + 1$ and the degeneracy exchanges between the neighboring sites, i.e., $g_{(I)}$ and $g_{(II)}$. Thus, we obtain Eq. (13). The energy-level splitting Δ affects the amount of moved degeneracy but not the amount of moved charge. Therefore, the thermopower strongly depends on Δ but the resistivity is not much affected by Δ as seen in Fig. 2.

Let us apply our theory to the thermopower in $NaCo_2O_4$. In the cobalt oxide, the transport is governed by $3d$ electrons in cobalt ions. Since the average valence of a cobalt ion in the stoichiometric compound is $+3.5$, the ratio of Co^{3+} and Co^{4+} ions is one, i.e., $x = 0.5$. The motion of an electron between neighboring Co^{3+} and Co^{4+} ions is accompanied with the change of ionic configuration from Co^{3+}-Co^{4+} to Co^{4+}-Co^{3+}. The Co^{3+} and Co^{4+} ions are identified with sites (II) and (I), respectively. Therefore, the high-temperature value of the thermopower is obtained by Eq. (13) with the degeneracies of Co^{3+} and Co^{4+} ions. It has been observed [13,14] that in the compound, Co^{3+} and Co^{4+} ions have the electronic configuration t_{2g}^6 and t_{2g}^5, respectively. These electronic configurations suggest that the degeneracies are 1 and 6 for Co^{3+} and Co^{4+} ions, respectively. Inserting these degeneracies into $g_{(I)}$ and $g_{(II)}$, respectively, and using $x = 0.5$, Eq. (13) gives 154 μV/K for the high-temperature value of the thermopower. Because the last term in Eq. (13) vanishes for $x = 0.5$, we conclude that the large thermopower in this compound is given by spin and orbital degrees of freedom.

Let us discuss a possibility of new thermoelectric materials in the transition metal oxides. We note the following remarkable features in $NaCo_2O_4$, namely, (i) the cobalt sites

form a triangular lattice, and (ii) the Co-O-Co bond angle is about 90°: Our theory shows that spin and orbital degrees of freedom cause the large thermopower through the degeneracy. In the transition metal oxides, however, there exist electron-phonon and superexchange interactions. These interactions are responsible for the long-range order in the spin and orbital degrees of freedom. They lift the spin and orbital degeneracy even at higher temperatures than the critical temperature of the long-range order forming a short-range correlation. The effects are considered to be harmful for the thermopower induced by the degeneracy, especially in the bipartite lattices. However, the triangular lattice gives frustration to spin and orbital degrees of freedom. The frustration prevents the electron-phonon and superexchange interactions from lifting the degeneracy. Thus, the triangular lattice structure is advantageous to the thermopower induced by the degeneracy. Although the effect of spin and orbital degrees of freedom on the thermopower has also been observed in some other doped transition metal oxides, the effects are smeared out with increasing hole concentration [15,16]. This is because the Coulomb interaction is less important in heavily doped systems than that in lightly doped ones. In order for spin and orbital to act as internal degrees of freedom on the thermopower, the strong Coulomb interaction (U) must exist on each site. The layered-hexagonal structure of $NaCo_2O_4$ with the Co-O-Co bond angle of about 90° provides the narrow electron band width (W) [17]. As a result, the parameter U/W is enhanced. Other layered-hexagonal cobalt oxides with large thermopower [18–21] satisfy the conditions. This is in strong contrast with the conventional guiding principle of thermoelectric materials [1,2]. Small angle of M-O-M bond (M denotes transition metal ion), narrow band, strong correlation of electrons, and frustration are the key ingredients to obtain thermoelectric materials in transition metal oxides.

In summary, we have studied the thermopower in strongly correlated electron systems with orbital degeneracy. By using the numerical diagonalization method on finite-size cluster, it was shown that the thermopower is strongly enhanced by the spin and orbital degeneracy, but the resistivity is not much affected by the degeneracy. The numerical method may be applied to the lower temperature region by using finite-temperature Lanczos method developed by Jaklič and Prelovšek [11]. Key ingredients to obtain thermoelectric materials in transition metal oxides have been proposed.

[1] G. Mahan, B. Sales, and J. Sharp, Phys. Today **50**, No. 3, 42 (1997).
[2] I. Terasaki, Y. Sasago, and K. Uchinokura, Phys. Rev. B **56**, R12 685 (1997).
[3] Y. Ando, N. Miyamoto, K. Segawa, T. Kawata, and I. Terasaki, Phys. Rev. B **60**, 10 580 (1999).
[4] P. M. Chaikin and G. Beni, Phys. Rev. B **13**, 647 (1976).
[5] A. Oguri and S. Maekawa, Phys. Rev. B **41**, 6977 (1990).
[6] J.-P. Doumerc, J. Solid State Chem. **109**, 419 (1994).
[7] D. B. Marsh and P. E. Parris, Phys. Rev. B **54**, 7720 (1996); **54**, 16 602 (1996).
[8] W. Koshibae, K. Tsutsui, and S. Maekawa, Phys. Rev. B **62**, 6869 (2000).
[9] G. Pálsson and G. Kotliar, Phys. Rev. Lett. **80**, 4775 (1998).
[10] J. Merino and R. H. McKenzie, Phys. Rev. B **61**, 7996 (2000).
[11] J. Jaklič and P. Prelovšek, Adv. Phys. **49**, 1 (2000).
[12] R. R. Heikes and R. W. Ure, Jr., *Thermoelectricity: Science and Engineering* (Interscience Publishers, New York, London, 1961).
[13] T. Tanaka, S. Nakamura, and S. Iida, Jpn. J. Appl. Phys. **33**, L581 (1994).
[14] R. Ray, A. Ghoshray, K. Ghoshray, and S. Nakamura, Phys. Rev. B **59**, 9454 (1999).
[15] A. B. Kaiser and C. Uher, *Studies of High Temperature Superconductors,* edited by A. V. Narlikar (Nova Science Publishers, New York, 1991), Vol. 7, p. 353.
[16] T. Okuda, K. Nakanishi, S. Miyasaka, and Y. Tokura, Phys. Rev. B **63**, 113104 (2001).
[17] D. J. Singh, Phys. Rev. B **61**, 13 397 (2000).
[18] T. Itoh and I. Terasaki, Jpn. J. Appl. Phys. **39**, 6658 (2000).
[19] I. Terasaki, in *Proceedings of the 18th International Conference on Thermoelectrics, Baltimore, MD, 1999* (IEEE, Piscataway, 2000), pp. 569–576.
[20] A. C. Masset, C. Michel, A. Maignan, M. Hervieu, O. Toulemonde, F. Studer, B. Raveau, and J. Hejtmanek, Phys. Rev. B **62**, 166 (2000).
[21] T. Yamamoto, I. Tsukada, K. Uchinokura, M. Takagi, T. Tsunobe, M. Ichihara, and K. Kobayashi, Jpn. J. Appl. Phys. **39**, L747 (2000); T. Yamamoto, Ph.D. Thesis, University of Tokyo, 2001.