Exact-diagonalization Study of Thermoelectric Response in Strongly Correlated Electron Systems

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Abstract

We have studied the thermopower and resistivity based on the Hubbard model with strong on-site Coulomb interaction and orbital degeneracy by using exact diagonalization method. It is shown that the thermopower is strongly enhanced by the spin and orbital degrees of freedom, but the resistivity is significantly less affected. The origin of the large thermopower in $NaCo_2O_4$ and a key for the strategy of new thermoelectric materials in transition metal oxides are proposed in the light of the theory.

Key words: thermopower; strongly correlated electron system; transition metal oxides

Since the discovery of the large thermopower in the lamellar cobalt oxide, $NaCo_2O_4$, by Terasaki *et al.* [1], the importance of thermoelectric response in transition metal oxides has been recognized in the development of new themoelectric materials. The materials generate electric energy from heat using thermoelectric-effect of solids. The temperature dependence of the in-plane resistivity of $NaCo_2O_4$ shows metallic behavior; the electrical resistivity (ρ) at 300 K is 200 $\mu\Omega$cm, i.e., this is a good metal. Although the thermopower in a good metal is expected to be small usually, the oxide shows large thermopower. The thermopower of the oxide increases with increasing temperature, and reaches 100 μV/K at 300 K.

In this paper, 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 cluster 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.

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The Hamiltonian in the strongly correlated electron systems with orbital degeneracy is expressed as;

$$H = -t\sum_{i\nu\sigma}(c^{\dagger}_{i,\nu,\sigma}c_{i+1,\nu,\sigma} + c^{\dagger}_{i+1,\nu,\sigma}c_{i,\nu,\sigma}) + \sum_{i,\nu}\Delta_{\nu}n_{i,\nu} + J\sum_{i,\nu}\mathbf{S}_{i\nu}\cdot\mathbf{S}_{i+1,\nu} + J_H\sum_{i}\mathbf{S}_{i,a}\cdot\mathbf{S}_{i,b}, \quad (1)$$

where ν (=a, b) and σ (=$\uparrow, \downarrow$) are the indices of orbital and spin, respectively. J_H is a strong ferromagnetic coupling. The energy-level splitting is given by $\Delta = \Delta_a - \Delta_b$. The effect of strong Coulomb interaction is taken into account by excluding the doubly occupied state in an orbital.

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

$$M^{1m} = -T\int_0^{\infty} dt \int_0^{1/k_BT} d\tau \mathrm{Tr}\left[\rho_0 \hat{j}_m(-t-i\tau)\hat{j}_1\right], \quad (3)$$

where $\hat{j}_l$'s are particle current (l=1) and energy flux (l=2) operators in the Heisenberg representation, respectively.

We diagonalize the Hamiltonian (1) on a periodic-chain with 6 unit-cells and 10 electrons using Householder method and calculate M's in Eq. (3) in the canonical formalism. The numerical results of the thermopower Q and electrical resistivity ρ ($= T/e^2M^{11}$) are shown in Fig. 1. The electrical resistivity and thermopower are increasing functions of temperature. The thermopower increases with decreasing Δ/t. On the other hand, the resistivity is almost independent of Δ/t. The thermopower is saturated at high temperatures and obeys the Heikes formula [2–7]:

$$Q = \frac{k_B}{e}\left(\ln g_{(\mathrm{I})} - \ln g_{(\mathrm{II})}\right) - \frac{k_B}{e}\ln\left(\frac{x}{1-x}\right), \qquad (4)$$

where $g_{(\mathrm{I})}$ ($g_{(\mathrm{II})}$) is the degeneracy of the site with an electron (the site with two electrons) and x is the hole concentration. The Δ dependence of the thermopower in Fig. 1 is clearly understood by Eq. (4): The degeneracies $g_{(\mathrm{I})}$ and $g_{(\mathrm{II})}$ originate from spin and orbital degrees of freedom. First, let us consider the case that t, $\Delta \ll k_BT \ll J_H$. In this case, on site (I), an electron is distributed to both orbitals and $g_{(\mathrm{I})}$ 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 $g_{(\mathrm{II})}$ 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 $g_{(\mathrm{I})}$ decreases with increasing Δ. It is expected that the suppression of $g_{(\mathrm{I})}$ causes the decrease in the thermopower through the first term in Eq. (4).

Let us apply our theory to $NaCo_2O_4$. It has been observed[8,9] that there exist Co^{3+} and Co^{4+} sites with the configurations of t_{2g}^6 and t_{2g}^5, respectively. The Co^{3+} and Co^{4+} ions are identified with (II) and (I), respectively. The electronic configurations of Co^{3+} and Co^{4+} suggests that $g_{(\mathrm{I})}$=6 and $g_{(\mathrm{II})}$=1. 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., $x = 0.5$. In this condition, Eq. (4) gives 154 μV/K for the high-temperature value of the thermopower. This result clearly shows why $NaCo_2O_4$ has the large thermopower with positive sign regardless of the high carrier-density. Because the last term in Eq. (4) vanishes for x=0.5, we conclude that the spin and orbital degrees of freedom based on the strong Coulomb interaction give rise to the large thermopower.

In the development of the conventional thermoelectric materials, attention has been paid on the charge degree of freedom of electrons in the thermoelectric response of solids. However, thermopower does not always reflect the charge degree of freedom. Our theoretical results show that the thermopower is strongly

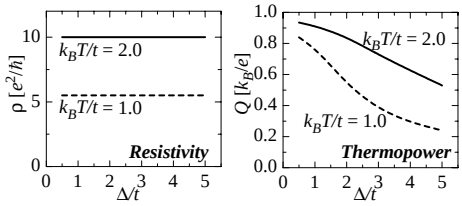

Fig. 1. Thermopower and resistivity as functions of Δ/t. J/t=0.25 and J_H/t=−10 are used.

enhanced by the spin and orbital degeneracy based on strong Coulomb interaction but the resistivity is not much affected. This will cause a great advantage to the development of the thermoelectric materials. We find the following remarkable features in $NaCo_2O_4$, namely, the cobalt sites form a triangular lattice and the Co-O-Co bond angle is about 90 degrees: 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 degrees provides the narrow electron band width (W) [10]. As a result, the parameter U/W is enhanced. The triangular lattice gives frustration to spin and orbital degrees of freedom. The frustration provides an environment where the degrees contribute to the thermopower more effective. Small angle of M–O–M bond (M denotes transiton metal ion), narrow band, strong correlation of electrons and frustration are the key ingredients to obtain thermoelectric materials in transition metal oxides.

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