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Thermopower in cobalt oxides

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We study theoretically the thermopower in cobalt oxides generalizing the Heikes formula. In the oxides, states of carriers are largely degenerate because the crystalline field and Hund's rule coupling compete in cobalt ions. It is shown that the degeneracy, together with strong correlation of $3d$ electrons, causes the large thermopower. The recent experiments in $NaCo_2O_4$ are discussed in the light of the theoretical result.

Recently, Terasaki *et al.*[1] have discovered large thermopower in the layered compound $NaCo_2O_4$, and proposed that the compound is of importance in view of potential application in thermoelectric devices which convert heat into energy. For application, not only the large value of Seebeck coefficient but also the low resistivity is required.[2] The Seebeck coefficient in $NaCo_2O_4$ 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 0.2 mΩ cm. These values observed at room temperature stand comparison with conventional thermoelectric materials composed of doped semiconductors.

Cobalt oxides are strongly correlated electron systems. In addition, $3d$ electrons have characteristic degeneracy due to spin and orbital degrees of freedom. Effects of the degeneracy have been studied theoretically and experimentally in $La_{1-x}Sr_xCoO_3$ with perovskite structure where each cobalt ion is surrounded by six oxygens,[3–12] and the competition between crystalline field and Hund's rule coupling is responsible for the degeneracy of the electronic states of a Co^{3+} (Co^{4+}) ion, i.e., low-spin (LS), intermediate-spin (IS), and high-spin (HS) states with the electronic configurations, t_{2g}^6 (t_{2g}^5), $t_{2g}^5e_g$ ($t_{2g}^4e_g$), and $t_{2g}^4e_g^2$ ($t_{2g}^3e_g^2$), respectively. The compound $NaCo_2O_4$ is of bronze type and has a layered structure where Na and CoO_2 layers are alternately stacked along the c axis. In the CoO_2 layers, each cobalt ion is surrounded by six oxygens as that in the perovskite cobalt oxide $La_{1-x}Sr_xCoO_3$. However, in $NaCo_2O_4$, cobalt ions form triangular lattices. Since the Co-O-Co bond angle is about 90°, the magnitude of the effective hopping of $3d$ electrons between neighboring Co sites may be much smaller than that in $La_{1-x}Sr_xCoO_3$. The average valence of a cobalt ion in stoichiometric $NaCo_2O_4$ is $+3.5$. It has been shown experimentally[13,14] that there exist magnetic Co^{4+} ions and nonmagnetic Co^{3+} ions with $S=0$ in $NaCo_2O_4$. The degeneracy of $3d$ electrons in cobalt ions is considered to play a crucial role in $NaCo_2O_4$ as well as $La_{1-x}Sr_xCoO_3$. The purpose of this paper is to show that the degeneracy of carriers, together with the strong electron correlation in cobalt oxides, brings about large thermopower.

Effects of the strong electron correlation on the thermopower have been theoretically studied by several authors[15–19] based on the Hubbard model. It was shown that the spin degeneracy induced by the strong correlation affects the thermopower. It was also shown that the thermopower at room temperature is actually close to that in high-temperature end of the data[16,18] in the parameter region which is appropriate to the transition-metal oxides. The high-temperature limit of the thermopower is given by Heikes formula.[15,20] When the Heikes formula gives a large value, the large thermopower at room temperature can be expected. Therefore we examine the thermopower at high temperatures generalizing the Heikes formula.[21] We will show that in cobalt oxides, not only the degeneracies of electronic states of Co^{3+} and Co^{4+} ions but also the ratio between them is important for the enhancement of thermopower.

Let us briefly review how the electron correlation causes the thermopower in the Hubbard model:[15]

$$H=t\sum_{\langle i,j\rangle\sigma}(c_{i\sigma}^{\dagger}c_{j\sigma}+\mathrm{H.c.})+U\sum_{i}n_{i\uparrow}n_{i\downarrow}, \tag{1}$$

where t is the transfer integral of an electron between neighboring sites, $c_{i\sigma}^{\dagger}$ and $c_{j\sigma}$ are creation and annihilation operators of electron with spin $\sigma(=\uparrow,\downarrow)$ at sites i and j, respectively, U is the on-site Coulomb interaction, and $n_{i\sigma}=c_{i\sigma}^{\dagger}c_{j\sigma}$. The Seebeck coefficient is expressed as

$$Q=\frac{1}{qT}\frac{M^{12}}{M^{11}}-\frac{\mu}{qT}, \tag{2}$$

where q is the charge of a carrier and μ is the chemical potential. In the present study, q is expressed as $-e$ where e is the absolute value of electron charge. M_{1i} $(i=1,2)$ is written as

$$M_{1i}=\int_0^{\infty}dt\int_0^{1/k_BT}d\tau\,\mathrm{Tr}[e^{-(H-\mu N)/k_BT}j_1(-t-i\tau)j_i], \tag{3}$$

where N is the number of electrons, and j_1 and j_2 are electric current and energy flux operators, respectively. We consider the high-temperature limit of thermopower in two cases, i.e., $t,U\ll k_BT$ and $t\ll k_BT\ll U$. In these cases, M_{1i}'s become constant and thus the first term in the right-hand side of Eq. (2) goes to zero. Therefore the thermopower is given by the chemical potential expressed as

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$$\frac{\mu}{T} = -\left(\frac{\partial s}{\partial N}\right)_{E,V}, \tag{4}$$

where s is the entropy of the system, and E and V are internal energy and volume. As $T \rightarrow \infty$ the entropy s is written as

$$s = k_B \ln g, \tag{5}$$

where g denotes the degeneracy. Inserting Eq. (5) into Eq. (4), we have

$$\frac{\mu}{k_B T} = -\left(\frac{\partial \ln g}{\partial N}\right)_{E,V}. \tag{6}$$

Then, the thermopower (2) in high-temperature limit is given by

$$Q = -\frac{k_B}{e}\frac{\partial \ln g}{\partial N}. \tag{7}$$

For $t, U \ll k_B T$, g is given by the total number of configurations,

$$g = \frac{(2N_A)!}{N!(2N_A - N)!}, \tag{8}$$

with N_A being the system size. Using Stirlings approximation and differentiating the term ln$g$ with respect to the total number of electrons, Eq. (7) is expressed as

$$Q = -\frac{k_B}{e}\ln\left(\frac{2-\rho}{\rho}\right), \tag{9}$$

with $\rho = N/N_A$. This is the generalized Heikes formula in the Hubbard model for $t, U \ll k_B T$. For $t \ll k_B T \ll U$, on the other hand, the configuration with doubly occupied state is excluded in g. Then, g is given by the number of configurations of charge without doubly occupied states and degeneracy of spin. We have

$$g = 2^N \frac{N_A!}{N!(N_A - N)!}. \tag{10}$$

As a result, the thermopower is expressed as

$$Q = -\frac{k_B}{e}\ln\left(2\frac{1-\rho}{\rho}\right). \tag{11}$$

In Eq. (11), the term, $-k_B/e \ln 2$, comes from the spin degree of freedom of an electron and the negative sign is due to the negative charge of an electron. The difference between Eqs. (9) and (11) is caused by the strong correlation.

Let us extend the theory mentioned above to cobalt oxides such as $NaCo_2O_4$ and $La_{1-x}Sr_xCoO_3$. We define the numbers of the configurations of Co^{3+} and Co^{4+} ions as g_3 and g_4, respectively. The values of g_3 and g_4 are determined by the Hund's rule coupling K, the crystal-field splitting Δ $(=10Dq)$ between e_g and t_{2g} levels and temperature T, as discussed below. Here, we take T to be sufficiently high.[22] The total number of the possible states g is given by the products of g_3, g_4, and the number of ways of arranging Co^{3+} and Co^{4+} sites which is given by $N_A!/M!(N_A - M)!$, where M is the number of Co^{4+} sites. Thus g is expressed as

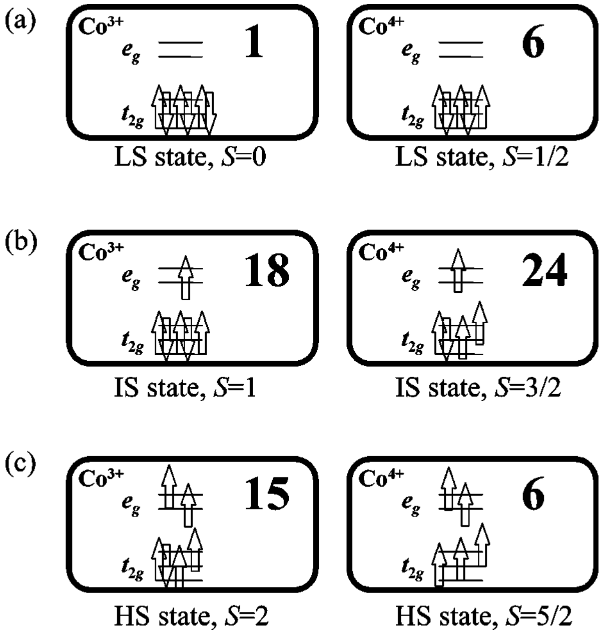

FIG. 1. Schematic representation of local states of cobalt ions, Co^{3+} and Co^{4+}. The lines indicate the energy levels of e_g and t_{2g} orbitals. The arrow represents a spin of an electron. (a) Low-spin state, (b) intermediate-spin state, (c) high-spin state. The magnitude of spin S is presented. The number in the frame denotes the degeneracy for each state.

$$g = g_3^{N_A - M} g_4^M \frac{N_A!}{M!(N_A - M)!}. \tag{12}$$

By inserting Eq. (12) into Eq. (7), the thermopower of the cobalt oxides is given by

$$Q = -\frac{k_B}{e}\ln\left(\frac{g_3}{g_4}\frac{x}{1-x}\right), \tag{13}$$

where $x(=M/N_A)$ is the concentration of Co^{4+} ions. Note that a Co^{4+} site has an extra charge of $+e$ compared with a Co^{3+} one and the dependence of Q on x in Eq. (13) is in contrast with that on ρ in Eq. (11). In Eq. (13), Q is a function of the ratio g_3/g_4. This indicates that the large absolute value of the thermopower can be realized when there exists an unbalance of the spin and orbital degrees of freedom between Co^{3+} and Co^{4+} sites.

We next examine the numbers of configurations g_3 and g_4 with respect to the parameters Δ, K, and T. In Co^{3+} and Co^{4+} sites, the LS, IS, and HS states are considered to be close in energy due to the competition between the Hund's rule coupling K and the crystal-field splitting Δ [see Fig. (1)]. Isolated Co^{3+} and Co^{4+} ions without crystal field have the HS states with $S=2$ and $\frac{5}{2}$, respectively, due to the coupling K. Introducing the octahedral crystal field, the energies of the LS and IS states decrease compared with that of the HS states. At a certain value of Δ, the LS state becomes the lowest in energy. The magnitude of Δ which gives the level crossing between HS and LS states in d^6 configurations of a Co^{3+} ion (Δ_3) is smaller than that of d^5 configurations of a Co^{4+} ion (Δ_4). In the following, we consider several cases for the degeneracies: (i) When the HS states of both Co^{3+}

TABLE I. The ratio g_3/g_4 in Eq. (13) in the cases (i)–(v). The obtained values of thermopower Q at $x=0.5$ are also presented.

	Co^{3+}	Co^{4+}	g_3/g_4	$Q(x=0.5)$
(i)	HS	HS	15/6	-79 μV/K
(ii)	HS+LS	HS	16/6	-84 μV/K
(iii)	LS	HS+LS	1/12	214 μV/K
(iv)	LS	LS	1/6	154 μV/K
(v)	HS+LS+IS	HS+LS+IS	34/36	5 μV/K

and Co^{4+} sites are stable $(k_BT \ll K;\Delta \ll K)$, g_3 and g_4 are 15 and 6, respectively. (ii) When the LS and HS states of a Co^{3+} site are close in energy and the HS state of a Co^{4+} site is stable $(k_BT \ll \Delta, K;\Delta \sim \Delta_3)$, g_3 is 16, which is obtained by the sum of the degeneracies of LS and HS states of Co^{3+} site, and $g_4=6$. (iii) When the LS states of a Co^{3+} site is stable and the LS and HS states of a Co^{4+} site are close in energy $(k_BT \ll \Delta, K;\Delta \sim \Delta_4)$, we have $g_3=1$ and $g_4=12$, which is given by the degeneracies of the LS and HS states of a Co^{4+} site. (iv) When the LS states of Co^{3+} and Co^{4+} sites are stable $(k_BT \ll \Delta;K \ll \Delta)$, g_3 and g_4 are 1 and 6, respectively. (v) When the LS, HS and IS states of Co^{3+} and Co^{4+} sites are close in energy,[23] g's are given by $g_3=1+18+15=34$ and $g_4=6+24+6=36$. The value of the ratio g_3/g_4 in Eq. (13) in each case is presented in Table I.

We apply Eq. (13) to the thermopower in $NaCo_2O_4$. Since the average valence of a cobalt ion in the stoichiometric compound is $+3.5$, we have $x=0.5$ and obtain the thermopower shown in Table I. The sign depends on the value of the ratio g_3/g_4. This means that not only the concentration x but also the ratio g_3/g_4 affect the sign of the thermopower. As seen in Table I, the case (iii) gives the largest value of the thermopower. Although there exist degeneracies in cobalt sites in the other cases, the thermopower is not always large. This is again because the thermopower in Eq. (13) is a function of g_3/g_4. The result can be understood as follows: When the ionic configuration changes from Co^{3+}–Co^{4+} to Co^{4+}–Co^{3+}, a charge moves to the neighboring site. At the same time, the configuration of the degeneracy changes from g_3–g_4 to g_4–g_3. Since the motion of the degeneracy causes the thermopower, the large value is obtained in the cases (iii) and (iv).

We have found that when the LS state is realized in a Co^{3+} site, the thermopower has the value of 214 μV/K [case (iii)] or 154 μV/K [case (iv)]. This explains the experiment,[1] since in $NaCo_2O_4$, Co^{3+} sites are in the LS state and Co^{4+} sites are magnetic.[13,14]

Finally, we discuss the thermopower in the doped RCoO$_3$ ($R=$La, Nd, Sm, Eu). The ground state of a cobalt ion in $LaCoO_3$ is the LS state with $S=0$, and the HS and IS states are close in energy to the LS state. It has been observed experimentally that the thermopower in $La_{1-x}Sr_xCoO_3$ with small $x(0<x<0.1)$ is strongly enhanced in the temperature region ($T\sim 100$–300 K).[4] Since the energy difference among the LS, IS, and HS states are order of 100 K in $LaCoO_3$, we consider that the degeneracy causes the enhanced thermopower in $La_{1-x}Sr_xCoO_3$. In RCoO$_3$ ($R=$Nd, Sm, Eu), on the other hand, the recent experiment[24] suggests that the LS state is stable. We therefore expect that the crucial difference appears in the thermopower between the doped RCoO$_3$ ($R=$Nd, Sm, Eu) and $La_{1-x}Sr_xCoO_3$. The experiment is highly desired.

In summary, we have studied thermopower in cobalt oxides generalizing the Heikes formula. In the oxides, three states of Co^{3+} and Co^{4+} sites, i.e., low-spin, intermediate-spin and high-spin states, are considered to be close in energy. It was shown that not only the large degeneracies in Co^{3+} and Co^{4+} sites but also the ratio between them is important for the enhancement of thermopower. In $NaCo_2O_4$, our theory suggests that the low-spin state of Co^{3+} sites bring about the large thermopower. The mechanism may be applied to the other systems.

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of 5 eV. We assume this value for NaCo2O4. As noted in the text, the magnitude of the effective hopping (t) between neighboring Co sites may be much smaller than that in $La_{1-x}Sr_xCoO_3$. Therefore we examine the electron system in the light of strong correlation ($t \ll U$).

[22] We examine the electronic state in the ionic model assuming that the exchange energy between Co^{3+} and Co^{4+} ions is small.

[23] The IS state is always the excited state in an isolated Co^{3+} or Co^{4+} ion. However, the kinetic energy terms can stabilize the IS states (Refs. 11 and 12). The case (v) is an example in which the values of g's include the degeneracies of IS states.

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