Negative Thermopower Induced by Entropy Backflow

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In the strongly correlated electron system, negative thermopower can be obtained by a mechanism that a net entropy flows along the opposite direction of the hole current. This "entropy-backflow" mechanism can make the thermopower of hole-doped conductor negative. We have synthesized $Ca(Mn_2Cu)Mn_4O_{12}$ in which a hole is doped by the substitution of Cu for Mn, and obtained -33 $\mu V/K$ at 1080 K. The value in the high temperature limit is estimated to be -79 ± 3 $\mu V/K$, which is qualitatively consistent with the theoretical prediction.

Key words: thermoelectric material, n-type conductor, entropy backflow, Mn oxide

1. INTRODUCTION

Since in 1997 the high thermoelectric performance was discovered in the layered Co oxide $NaCo_2O_4$[1], the strongly correlated electron systems have been studied extensively as a possible candidate for a thermoelectric material. Following $NaCo_2O_4$, other layered Co oxides, Ca-Co-O[2] and Bi-Sr-Co-O[3] have been found to have a good thermoelectric performance.

The conversion efficiency of a thermoelectric material is characterized by the figure of merit $Z = S^2/\rho\kappa$, where S, ρ and κ are the thermopower, the resistivity, and the thermal conductivity, respectively. Consequently a good thermoelectric material has the large S, the small ρ and κ. Funahashi *et al.* reported that the maximum of the dimensionless figure of merit ZT is larger than 1.2 at 1000 K for Ca-Co-O[2], which means that the layered cobalt oxides might be the best family among all the thermoelectric materials.

Thermoelectric devices are made from a couple of p and n-type thermoelectric materials. $NaCo_2O_4$ is a p-type thermoelectric oxide, and there are no n-type thermoelectric oxides comparable with $NaCo_2O_4$. In addition, n-type conductors themselves are fewer in number than p-type conductors in the transition-metal oxides. In the strongly correlated electron systems, however, a negative thermopower can be obtained in a hole-doped system. Their thermopower in high-temperature limit is expressed as [4],

$$S = \frac{k_B}{e} \ln \frac{g_A}{g_B} \frac{p}{1-p}, \quad (1)$$

where g_A and g_B represent the degeneracy of the site configurations of A and B ions, respectively. p represents the concentration of the B ion. This equation is a generalized Heikes formula[5], and explains the large thermopower of the layered Co oxides. According to this equation, we can obtain a negative thermopower through the term of $-k_B/e \cdot \ln(g_A/g_B)$ in a hole-doped system if $g_A > g_B$.

Perovskite Mn oxides have Mn^{3+} and Mn^{4+} ions of the high-spin state (HS), which can be a good test for Eq.(1). Mn^{3+} (HS) has the electron configuration of $(t_{2g})^3(e_g)^1$ with the spin S=2. Thus $g_{Mn^{3+}}$ is calculated to be 10, where 5 comes from S, and 2 comes from e_g orbitals. Similarly $g_{Mn^{4+}}$ is calculated to be 4. From these number, S is calculated to be $-k_B/e \cdot \ln(10/4) = -79$ $\mu V/K$ when $p=0.5$. This negative thermopower is caused by a mechanism that the net entropy flows along the opposite direction of the hole current (see Fig. 1). This "entropy-backflow" mechanism can make the thermopower of hole-doped conductor negative.

We synthesized $Ca(Mn_2Cu)Mn_4O_{12}(x=0, 1)$ in which a hole is doped by the substitution Cu for Mn. Why we selected this system is that a crystal structure of $Ca(Mn_2Cu)Mn_4O_{12}$ is cubic, and e_g orbital is expected to be degenerate. In addition, Mn^{3+} and Mn^{4+} exist in $Ca(Mn_2Cu)Mn_4O_{12}$ by 1:1, where Eq.(1) reduces to $-k_B/e \cdot \ln(g_A/g_B)$. Note that other perovskite manganites with $Mn^{3+}:Mn^{4+}=1:1$ are unstable against charge ordering. Therefore in this system, we expect the negative thermopower by the exchange Mn^{4+} for Mn^{3+}. The purpose of this paper is to show the negative large

current flow $+e$
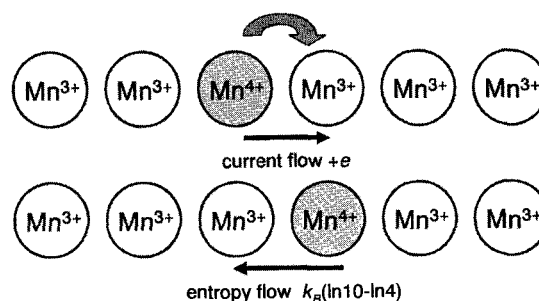
entropy flow $k_B(\ln 10 - \ln 4)$

Fig. 1 Schematic view of the mechanism of the negative thermoelectric power in the hole-doped Mn oxide.

thermopower by entropy backflow.

2. EXPERIMENT

Polycrystalline samples of $Ca(Mn_2Cu)Mn_4O_{12}$ was prepared by a solid-state reaction. Stoichiometric amounts of $CaCO_3$, Mn_3O_4 and CuO were mixed, and the mixture was calcined at 870 °C. The product was finely ground, pressed into a pellet, and sintered at 930 °C for 12 h in air. The X-ray diffraction (XRD) of the sample was measured using a standard diffractometer with Fe $K\alpha$ radiation as an X-ray source in the θ-2θ scan mode. All the peaks are indexed as the $Ca(Mn_2Cu)Mn_4O_{12}$ [6] as shown in Fig. 2.

The thermopower was measured using a steady-state technique, below room temperature in a liquid He cryostat, and above room temperature in an electric furnace. A temperature gradient of 0.5 K/mm was generated by a small resistive heater pasted on one edge of a sample below 500 K and by cooling one edge of a sample by an air pump above 500 K, and was monitored by a differential thermocouple made of copper-constantan below room temperature, and by that of platinum-rhodium above room temperature. The thermopower of the voltage leads was carefully subtracted.

3. RESULT AND DISCUSSION

Figure 3 shows the crystal structure of $Ca(Mn_{3-x}Cu_x)Mn_4O_{12}$ ($x=0$, 1). The large light spheres, the dark spheres, and the octahedra represent Ca, Mn (Cu), and MnO_6, respectively. The crystal symmetry is cubic with a doubling of the ideal ABO_3 perovskite cell. The doubling of the unit cell is due to the ordering of the Ca and Mn(Cu) ions and a tilted three-dimensional network of MnO_6 octahedra sharing corners. The Mn-O-Mn angle is about 142°, because of Cu^{2+} and Mn^{3+} having a small ionic radius for A site.

Figure 4 shows the thermopower of $Ca(Mn_2Cu)Mn_4O_{12}$. The inset schematically shows the electron configuration of Mn^{3+} and Mn^{4+} and the two dotted lines give the thermopower at the high-temperature limit, respectively. At 220 K, the thermopower becomes from positive to negative in spite of hole-doped system. Resistivity of $Ca(Mn_{3-x}Cu_x)Mn_4O_{12}$ decreases with incresing x as shown in ref. [7], which strongly suggests that the substitution of Cu^{2+} for Mn^{3+} supplies a hole in the system. From 100 to 500 K, the thermopower changes slowly, and from 500 to 800 K the thermopower stays near -27 $\mu V/K$. This value is very close to $-k_B/e \cdot \ln(5/4) = -20$ $\mu V/K$. As shown in the inset of Fig. 4, $\ln(5/4)$ is expected for non-degenerate e_g orbitals. The splitting energy of e_g orbitals will be larger than 800 K, and the thermopower begins to deviate from -27 $\mu V/K$ above 800 K. Eventually it reaches -33 $\mu V/K$ at 1080 K, and goes towards -79 ± 3 $\mu V/K$ as $T \to 8$. This value is nearly equal to $-k_B/e \cdot \ln(10/4) = -79$ $\mu V/K$ of the theoretical prediction. This implies that as the temperature becomes high, the degree of freedom of the e_g orbital recovers. Palstra *et al.* estimated that the high-temperature-limit thermopower of $La_{1-x}Ca_xMnO_3$ was -20 $\mu V/K$ ($= -k_B/e \cdot \ln(5/4)$) [8]. We think that their measured temperature was not high enough to find the degeneracy of e_g orbital. This indicates that the
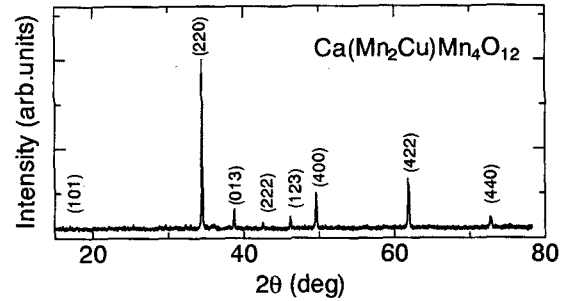

Fig. 2 The X-ray diffraction pattern of $Ca(Mn_2Cu)Mn_4O_{12}$
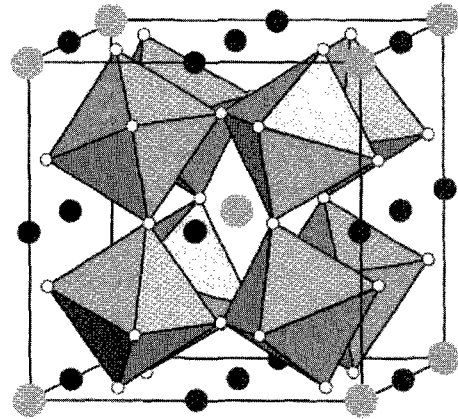

Fig. 3 The crystal structure of $Ca(Mn_{3-x}Cu_x)Mn_4O_{12}$. The large light spheres, the dark spheres, and the octahedra represent Ca, Mn (Cu), and MnO_6, respectively.

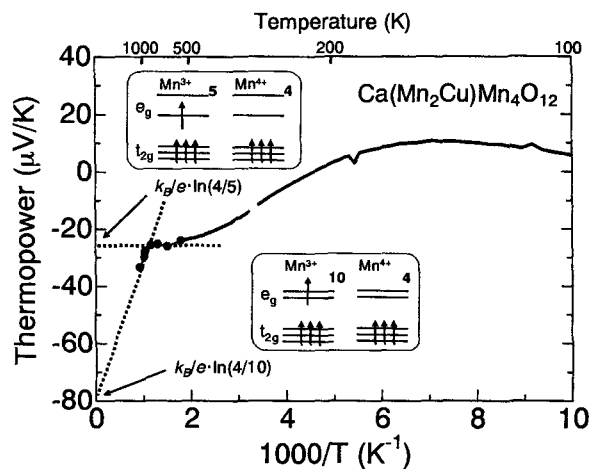Fig. 4 The thermopower of high-temperature limit of $Ca(Mn_2Cu)Mn_4O_{12}$. The insets show the configurations of Mn^{3+} and Mn^{4+} at the temperature, respectively.

thermopowerof $Ca(Mn_{3-x}Cu_x)Mn_4O_{12}$ is affected by the degeneracy of e_g orbital as well as the degeneracy of the spin.

4. SUMMARY

We synthesized $Ca(Mn_2Cu)Mn_4O_{12}$ in which a hole is doped by the substitution Cu for Mn. $Mn^{3+}:Mn^{4+}=1:1$ is realized, where $-k_B/e \cdot \ln(g_A/g_B)$ is expected to be -79 $\mu V/K$. The thermopower of $Ca(Mn_2Cu)Mn_4O_{12}$ is

observed to be $-33\,\mu$V/K at 1080 K and about -79 ± 3 μV/K as $T{\to}8$, which is quantitatively consistent with the theoretical prediction. This negative thermopower is caused by a mechanism that the net entropy flows along the opposite direction of the hole current. This "entropy-backflow" mechanism can make the thermopower of hole-doped conductor negative.

ACKNOWLEDGEMENTS

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