Universal charge transport of the Mn oxides in the high temperature limit

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We have found that various Mn oxides have the universal resistivity and thermopower in the high temperature limit. The resistivities and thermopowers of all the samples go toward constant values of 7±1 mΩcm and −79±3 μV/K, which are independent of carrier density and crystal structures. We propose that the electric conduction occurs in a highly localized way in the high temperature limit, where the exchange of entropy and charge occurs in the neighboring Mn\textsuperscript{4+} and Mn\textsuperscript{3+} ions.

INTRODUCTION

In condensed matter physics, many researches have focused on low-temperature physics. Superconductivity, Anderson localization, superfluidity, metal-insulator transition, and Kondo effect are typical low-temperature physics. In contrast, studies on high-temperature physics are fewer in number at present.

Recently, magnetic oxides have been studied extensively as a possible candidate for thermoelectric materials at high temperatures since the discovery of large thermopower in NaCo\textsubscript{2}O\textsubscript{4} \textsuperscript{[1, 2]}. The high thermoelectric performance of NaCo\textsubscript{2}O\textsubscript{4} is currently explained in terms of a large degeneracy of spin and orbital degrees of freedom of Co\textsuperscript{3+} ions \textsuperscript{[3]}. Therefore, control of spin and orbital states of magnetic ions would improve the performance of thermoelectric oxides. In this sense, thermoelectrics can be a new research direction in magnetics.

We hope that new physical phenomena such as the good thermoelectricity in NaCo\textsubscript{2}O\textsubscript{4} might exist in magnetic materials at high temperatures. Here we have paid attention to the transport properties of Mn oxides, where a complicated electron-spin-phonon interaction induces an exotic electric conduction such as colossal magnetoresistance. We have measured their resistivity and thermopower up to 1000 K, and have found that they are essentially independent of carrier density and crystal structure in the high temperature limit. This is quite anomalous in the sense that thermopower and resistivity usually depend on carrier density and crystal structure for conventional metals and semiconductors.

EXPERIMENT

Polycrystalline samples of Ca(\textsubscript{Mn}\textsubscript{1−x}Cu\textsubscript{x})Mn\textsubscript{4}O\textsubscript{12} \((x = 0, 0.25, 0.5, 0.75 \text{ and } 1)\) and LiMn\textsubscript{2}O\textsubscript{4} were prepared by a solid-state reaction. Stoichiometric amounts of CaCO\textsubscript{3}, Mn\textsubscript{3}O\textsubscript{4}, CuO, and Li\textsubscript{2}CO\textsubscript{3} were mixed, and the mixture was calcined at 900°C for 12 h for CaMn\textsubscript{3}Mn\textsubscript{4}O\textsubscript{12}, 870°C for 12 h for Ca(\textsubscript{Mn}\textsubscript{1−x}Cu\textsubscript{x})Mn\textsubscript{4}O\textsubscript{12} \((x > 0)\), and 800°C for 24 h for LiMn\textsubscript{2}O\textsubscript{4}. The product was finely ground, pressed into a pellet, and sintered at 950°C for 72 h for CaMn\textsubscript{3}Mn\textsubscript{4}O\textsubscript{12}, 930°C for 12 h for Ca(\textsubscript{Mn}\textsubscript{1−x}Cu\textsubscript{x})Mn\textsubscript{4}O\textsubscript{12} \((x > 0)\), and 850°C for 24 h for LiMn\textsubscript{2}O\textsubscript{4}. All the samples were calcined in air.

Single crystals of Pr\textsubscript{0.5}Ca\textsubscript{0.5}Mn\textsubscript{3}O\textsubscript{4} were grown using the traveling solvent floating zone method. Stoichiometric amounts of Pr\textsubscript{2}O\textsubscript{3}, CaCO\textsubscript{3}, and MnO\textsubscript{2} were mixed, and the mixture was calcined at 1200°C for 8 h in air. The calcined powder was ground, placed into a rubber tube and then hydrostatically pressed under 2000 kg/cm\textsuperscript{2}. The pressed rod was sintered at 1350°C for 12 h in air. The feed and seed rods were rotated in opposite directions at a relative rate of 40 rpm and the melted zone was vertically scanned at a speed of 7 mm/h. The growth atmosphere was air.

The X-ray diffraction (XRD) of the samples was measured using a standard diffractometer with Fe Kα radiation as an X-ray source in the θ-2θ scan mode. The resistivity was measured by a four-probe method, below room temperature (4.2-300 K) in a liquid He cryostat, and above room temperature (300-1000 K) in an electric furnace. The thermopower was measured using a steady-state technique, below room temperature (4.2-300 K) in a liquid He cryostat, and above room temperature (300-1080 K) 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.

RESULTS AND DISCUSSION

Figure 1 shows typical X-ray diffraction patterns of (a) Ca(\textsubscript{Mn}2Cu)Mn\textsubscript{4}O\textsubscript{12} and (b) LiMn\textsubscript{2}O\textsubscript{4}. The samples were successfully prepared as single phases, and all the peaks are indexed \textsuperscript{[4, 5]}. Although crystal structures are
FIG. 1: X-ray diffraction patterns of (a) Ca(Mn$_{2}$Cu)Mn$_{4}$O$_{12}$ and (b) LiMn$_{2}$O$_{4}$.

different among Ca(Mn$_{3-x}$Cu$_{x}$)Mn$_{4}$O$_{12}$ (CaCu$_{3}$Ti$_{4}$O$_{12}$-type), Pr$_{0.5}$Ca$_{0.5}$MnO$_{3}$ (GdFeO$_{3}$-type) and LiMn$_{2}$O$_{4}$ (spinel), they share a common feature that the Mn ions in the conduction path are either trivalent (Mn$^{3+}$) or tetravalent (Mn$^{4+}$) in the high-spin state, being surrounded by the oxygen octahedron. The Mn$^{3+}$ ion has one d electron in the doubly degenerate eg level, and the oxygen octahedron is elongated in one direction to release the degeneracy through the Jahn-Teller effect. In contrast, the Mn$^{4+}$ ion has no Jahn-Teller effect, and is stable in the undistorted octahedron. Thus, when a hole hops from Mn$^{4+}$ to Mn$^{3+}$, it inevitably accompanies the elongation of the oxygen octahedra, forming a small polaron.

Figure 2 shows the resistivities of the Mn oxides. An important feature of the small-polaron conductor is that the mobility obeys an activation-type temperature dependence, where the activation energy is the binding energy of the polaron (the Jahn-Teller distortion energy or the eg level splitting in the present case). Then the resistivity is described by the activation transport as

$$\rho = \rho_0 \exp(E_\rho/k_BT),$$

where $E_\rho$ is the activation energy seen in the resistivity. As is clearly shown in Fig. 2, all the resistivities are well described by the activation process. Some of the resistivities show an abrupt increase below a certain temperature, which is due to the charge-ordering transition. The transition temperature and the resistivity jump are consistent with those in the literature [6, 7]. Above the transition temperature, Mn$^{3+}$ and Mn$^{4+}$ are randomly distributed, where the polaron energy is determined by the Jahn-Teller distortion of a single ion. On the contrary, Mn$^{3+}$ and Mn$^{4+}$ are ordered below the transition temperature, where the polaron energy is modified by the collective Jahn-Teller effect.

We examined a least-square fitting with Eq. (1), as shown in the dotted lines in Fig. 2. Note that we used the data only above the transition temperature for the charge-ordered samples. As is clearly shown, the extrapolated values $\rho_0$ are in the range from 6 to 8 mΩcm. Note that resistivity of solids can vary in a wide range.

FIG. 2: Temperature dependence of the resistivities of various Mn oxides. The dotted lines are fitting curves by Eq. (1).

FIG. 3: (a) Temperature dependence of the thermopowers of various Mn oxides. The dotted lines are fitting curves by Eq. (5). The data for LiMn$_{2}$O$_{4}$ is taken from Ref. [9]. (b) Electron configuration in Mn ions.
from $10^{-6}$ (copper metal) to $10^{20}$ (silica) Ωcm. In this sense, we can safely approximate $7 \pm 1$ mΩcm as a constant value.

This result is quite anomalous. Resistivity in the high temperature limit is known as the Ioffe-Regel limit (or Mott’s minimum conductivity), where the mean free path is nearly equal to the lattice constant ($a$). The resistivity is equal to

$$\rho = \frac{3\pi^2 k_F}{e^2 a k_F},$$  \hspace{1cm} (2)

where $k_F$ is Fermi wave vector in a three-dimensional case. Thus the high-temperature resistivity is dependent on carrier density and crystal structure through $k_F$ and $a$. Then $\rho_0$ is calculated to be 2 mΩcm for $k_F=\pi/2a$ (Mn$^{3+}$:Mn$^{4+}=1:1$) and $a=0.4 \text{ nm}$ (a typical Mn-O-Mn distance of our samples), which is reasonably close to the observed value of $7 \pm 1$ mΩcm.

Figure 3(a) shows the thermopowers of all the samples. All the data merge near $-25 \text{ }\mu\text{V/K}$ around 800-1000 K. Note that the thermopower for LiMn$_2$O$_4$ is taken from Ref. [3]. Koshiba et al. [3] have proposed that thermopower of the transition-metal oxides in the high temperature limit is described by an extended Heikes formula written as

$$S = -\frac{k_B}{q} \ln \left( \frac{g_A}{g_B} \frac{p}{1-p} \right),$$  \hspace{1cm} (3)

where $g_i$ is the degeneracy of the electron configuration on the $i$ ions, and $p$ the concentration of the B ion, and $q$ is the charge difference between the A and B ions. According to Eq. (3), we calculate the thermopower for Mn$^{3+}$:Mn$^{4+}=1:1$ ($p=0.5$) as

$$S = -\frac{k_B}{|e|} \ln \left( \frac{g_{\text{Mn}^{3+}}}{g_{\text{Mn}^{4+}}} \right).$$  \hspace{1cm} (4)

The Mn$^{3+}$ and Mn$^{4+}$ ions in the Mn oxides are in the high-spin state, where Mn$^{3+}$ has the electron configuration of $(t_{2g})^3(e_g)^1$ as shown in the inset of Fig. 2. Near 800 K, $E_\rho$ is larger than $k_BT$, which implies that the Jahn-Teller distortion is effective for the polaron formation. Thus the $e_g$ level splitting is valid (no orbital degeneracy), and $g_{\text{Mn}^{3+}}$ should be equal to 5 owing only to the spin degeneracy of $S=2$ (see Fig. 3(b)). Since the Mn$^{4+}$ ion $(t_{2g})^3$ has no orbital degeneracy, $g_{\text{Mn}^{4+}}$ is equal to 4 owing to $S=3/2$. Then the thermopower is evaluated to be $-k_B \ln(5/4)/|e| = -20 \mu\text{V/K}$, which is in good agreement with the observed value of $-25 \mu\text{V/K}$. Similar results for (La$_{1-x}$Ca$_x$)MnO$_3$ were reported by Palstra et al. [10].

Above 1000 K, the thermopowers begin to decrease, and seem to approach $-79 \pm 3 \text{ }\mu\text{V/K}$ as $T \rightarrow \infty$ [11]. For high-temperature extrapolation, we assumed the expression for a high-temperature thermopower as

$$S = S_0 + \frac{k_B}{q} \frac{E_S}{k_BT}.$$  \hspace{1cm} (5)

where $E_S \ (E_\rho \gg E_S)$ is a characteristic energy for $S$, and $S_0$ is the thermopower in the high-temperature limit [10]. The physical meaning is simple: the $e_g$-orbital degeneracy recovers above 1000 K, where $g_{\text{Mn}^{3+}} = 10$ and $S = -k_B \ln(10/4)/|e| \sim -79 \text{ }\mu\text{V/K}$ are expected, as shown in Fig. 3(b).

In the above argument, we evaluated the high-temperature resistivity and thermopower for Mn$^{3+}$:Mn$^{4+}=1:1$. This is the case for Ca(Mn$_3$Cu)Mn$_4$O$_{12}$, LiMn$_2$O$_4$, and Pr$_{0.5}$Ca$_{0.5}$MnO$_3$, but is not applicable to Ca(Mn$_{3-x}$Cu$_x$)Mn$_4$O$_{12}$ ($x<1$). However, the observed $\rho$ and $S$ seem to have universal values for $T \rightarrow \infty$ regardless of the Mn$^{4+}$ content or the carrier density. We do not have a clear answer for this yet, but propose a possible scenario that the electric conduction occurs in a highly localized way in the high temperature limit, where the exchange of entropy and charge occurs in the neighboring Mn$^{3+}$ and Mn$^{4+}$ ions. Figure 4 schematically shows a local exchange Mn$^{3+}$ for Mn$^{4+}$. Suppose conduction occurs in a filamentary path of the Mn$^{4+}$ motion. Then the Mn$^{4+}$ ion induces the thermopower of $S = -k_B \ln(10/4)/|e|$ with $\rho_0 = 2$ mΩcm, every time it replaces the Mn$^{3+}$ site. We think this phenomena would occur not only in the Mn oxides but also in other small-polaron conductors in general.

**SUMMARY**

We prepared various Mn oxides consisting of Mn$^{3+}$ and Mn$^{4+}$ ions in the MnO$_6$ octahedron, and measured their resistivity and thermopower from 4 to 1000 K. Most unexpectedly, we have found that they seem to have unique asymptotic values in the high temperature limit. We have explained this in terms of the local ion exchange between Mn$^{3+}$ and Mn$^{4+}$.

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![Schematic picture of electric conduction of Mn oxides](image-url)
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