

Seebeck Coefficient in the System $(\text{Gd}_{1-x}\text{Ca}_x)\text{MnO}_{2.98}$ ($0.6 \leq x \leq 0.95$)

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The Seebeck coefficient (S) of the perovskite system $(\text{Gd}_{1-x}\text{Ca}_x)\text{MnO}_{2.98}$ ($0.6 \leq x \leq 0.95$) was measured in the temperature range 100 to 350 K. S is negative and temperature-independent at high temperature. The temperature-independent region extends to lower temperatures with increasing x . In the region $0.8 \leq x \leq 0.95$, the low- and the high-spin states of Mn^{3+} coexist. The temperature independence of S is explained by the hopping model. In the range $0.6 \leq x < 0.8$, the spin state of the Mn^{3+} ion changes from low to high at a metal–insulator transition temperature (T_i). A monotonous change of S corresponds to the change from a semiconductor to a metal. © 1991 Academic Press, Inc.

The electrical resistivity of perovskite-type $(\text{Ln}_{1-x}\text{Ca}_x)\text{MnO}_3$ (Ln : La, Nd, and Gd) was measured by Taguchi *et al.* (1–3). These manganates are n -type semiconductors below room temperature. At low temperature, the electrical resistivity (ρ) nonlinearly decreases with increasing temperature. It follows Mott's $T^{-1/4}$ law, indicating the possible occurrence of variable range hopping of electrons due to Anderson localization (4). At high temperature, ρ has a positive temperature coefficient ($d\rho/dT > 0$), and a metal–insulator transition occurs without any crystallographic change. A metal–insulator transition temperature (T_i) across which $d\rho/dT$ changes from negative to positive decreases with increasing x .

At a particular value of x in $(\text{Ln}_{1-x}\text{Ca}_x)$

MnO_3 , T_i increases with increasing ionic radius of the rare earth ion. In the perovskite $(\text{Nd}_{0.1}\text{Ca}_{0.9-x}\text{Sr}_x)\text{MnO}_{2.97}$, both the number of $4f$ electrons of the rare earth ion and the $\text{Mn}^{3+}/\text{Mn}^{4+}$ ratio are independent of x , but T_i increases linearly with increasing x . Because of the difference of the ionic radius between Ca^{2+} and Sr^{2+} ions, the cell constants increase with increasing x (5). These facts suggest that T_i obviously increases with increasing Mn–O distance in these perovskites.

The effective magnetic moment (μ_{eff}) of $(\text{Ln}_{1-x}\text{Ca}_x)\text{MnO}_3$ (Ln : La, Nd, and Gd) suggests that the electron configuration of the Mn^{3+} ion changes from a low-spin state $(d\varepsilon)^4(d\gamma)^0$ to a high-spin state $(d\varepsilon)^3(d\gamma)^1$ at T_i , and that this change of the spin state of the Mn^{3+} ion causes the metal–insulator transition. But μ_{eff} calculated from the linear part of the magnetic susceptibility vs tem-

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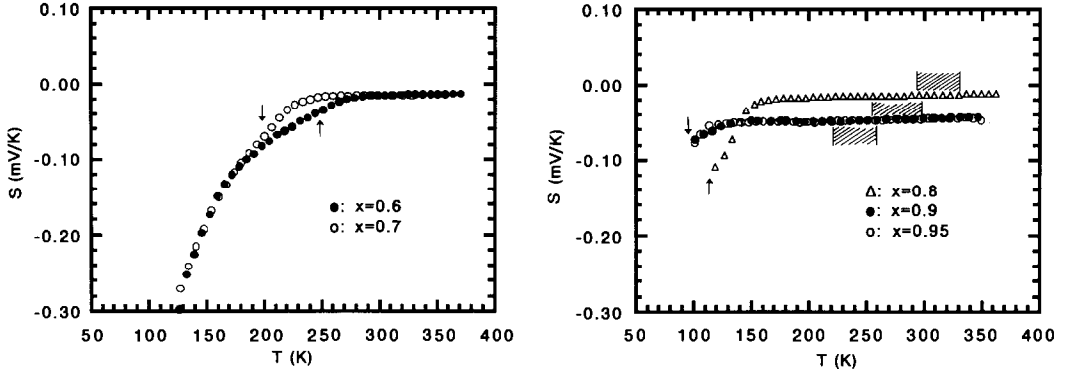


FIG. 1. The Seebeck coefficient (S) vs temperature for the system $(\text{Gd}_{1-x}\text{Ca}_x)\text{MnO}_{2.98}$. The hatching indicates the metal-insulator transition temperature (T_i). The arrow indicates the temperature (T_d) of the deviation from Mott's $T^{-1/4}$ law.

perature below and above T_i deviates slightly from the theoretical value. For example, in $(\text{Gd}_{1-x}\text{Ca}_x)\text{MnO}_{2.98}$ ($0.8 \leq x \leq 0.9$), the observed μ_{eff} in the metal region is lower than both the theoretical values in the metal region and the theoretical values in the insulator regions. In the present study, we measured the Seebeck coefficient (S) of $(\text{Gd}_{1-x}\text{Ca}_x)\text{MnO}_{2.98}$. These results provide information that clarifies the deviation of μ_{eff} from the theoretical values and the mechanism of the metal-insulator transition in these perovskites.

The preparation of $(\text{Gd}_{1-x}\text{Ca}_x)\text{MnO}_{2.98}$ ($0.6 \leq x \leq 0.95$) was described in detail elsewhere (3). A measurement was carried out under a slow heating rate (2.5 K/min). Figure 1 shows the relation between S and temperature. S is negative and temperature-independent at high temperature with the values $S = -10$ to $15 \mu\text{V/K}$ for $0.6 \leq x \leq 0.8$ and -40 to $50 \mu\text{V/K}$ for $0.9 \leq x \leq 0.95$. This temperature-independent region extends to lower temperature with increasing x . The hatching indicates T_i for $0.8 \leq x \leq 0.95$, but T_i for $0.6 \leq x \leq 0.7$ is above 400 K. As seen in Fig. 1, there is no remarkable change in S at T_i . The arrows in Fig. 1 show the temperature (T_d) of the deviation from Mott's $T^{-1/4}$ law (3). The temperature-inde-

pendent region appears above $T_d + (30 \text{ to } 40 \text{ K})$.

In the range $0.6 \leq x < 0.8$, the observed μ_{eff} agrees with the theoretical value, i.e., the spin state of Mn^{3+} changes from low (localized or semiconductive) to high (collective or metallic). On the other hand, in the range $0.8 \leq x \leq 0.95$, the observed μ_{eff} in the metal region is smaller than the theoretical high-spin value, and nearly equal to the theoretical μ_{eff} in the low-spin region (3). We think that part of the Mn^{3+} ions don't change their spin state above T_i . Both the low-spin state (a semiconductive part) and the high-spin state (a metallic part) of Mn^{3+} ions coexist above T_i .

Figure 2 shows the schematic illustration of the electrical conductivity (σ) of $(\text{Gd}_{1-x}\text{Ca}_x)\text{MnO}_{2.98}$. In Fig. 2, there are five curves (I, II, III, IV, and V). At low temperature, σ follows a variable-range hopping of electrons due to Anderson localization and is given by

$$\sigma = A \exp(-B/T^{1/4}), \quad (1)$$

where A and B are constants (curve I) (6). With increasing temperature, σ deviates from Mott's $T^{-1/4}$ law due to thermal excitation from E_F (Fermi energy) to E_C (critical energy) of the mobility edge. σ is given by

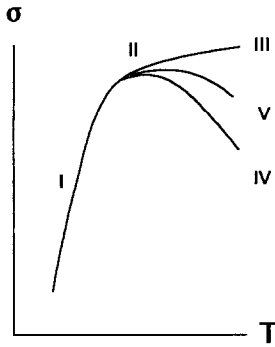


FIG. 2. Schematic illustration of the electrical conductivity (σ) vs temperature curve for the system $(\text{Gd}_{1-x}\text{Ca}_x)\text{MnO}_{2.98}$.

$$\sigma = A' \exp\{-(E_C - E_F)/kT\}, \quad (2)$$

where A' is a constant and k is the Boltzmann constant (curve II) (6). If the low-spin state of the Mn^{3+} ion (the semiconductive part) remains, σ follows Eq. (2) at high temperature (curve III). If the Mn^{3+} ion changes from the low-spin state (the semiconductive part) to the high-spin state (the metallic part) at high temperature, σ is generally given by

$$\sigma = A''/T, \quad (3)$$

where A'' is a constant (curve IV). In the region $0.6 \leq x < 0.8$, σ follows curves I \rightarrow II \rightarrow IV. On the other hand, in the range $0.8 \leq x \leq 0.95$, the semiconductive and metallic part coexist at high temperature. The observed σ is between curves III and IV (curve V), and σ follows curves I \rightarrow II \rightarrow V.

The ρ of $\text{Na}_{0.33}\text{V}_2\text{O}_5$ follows Mott's $T^{-1/3}$ law indicating a variable range hopping of the electrons due to Anderson localization (7). Jerome and Sienko reported that S of $\text{Na}_{0.33}\text{V}_2\text{O}_5$ is negative and temperature-independent in the temperature range 140–500 K (8). They calculated S by using the hopping model. At low temperature ($kT \ll -E_D$), S is given by

$$S = -(k/e)\{E_D/kT + \ln(n/N_D) + C\}, \quad (4)$$

where e is the electron charge, E_D is a donor energy, N_D is the total number of donor centers, n is the total number of electrons distributed over the N_D donor states, and C is a constant. S exponentially changes with increasing temperature. At high temperature ($kT \gg -E_D$), S is given by

$$S = -(k/e)\{\ln\{n/(N_D + N_C)\} + C'\}, \quad (5)$$

where N_C is the total number of conduction states, and C' is a constant. S is independent of temperature and depends on the value of $n/(N_D + N_C)$. On the other hand, S of the metal is generally given by

$$S = -(k/e)\pi^2 k(T/E_F), \quad (6)$$

and is very small and changes linearly with temperature (9). Figure 3 shows the schematic illustration of S . In Fig. 3, there are three curves (I, II, and III) which correspond to Eqs. (4), (5), and (6), respectively.

By using their hopping model, we qualitatively explain S of $(\text{Gd}_{1-x}\text{Ca}_x)\text{MnO}_{2.98}$. At low temperature, the electrical conductivity follows Mott's $T^{-1/4}$ law and S exponentially changes with increasing temperature (curve I). At T_d , the electrical conductivity deviates from Mott's $T^{-1/4}$ law and S is temperature-independent above $T_d + (30 \text{ to } 40 \text{ K})$ (curve II). E_D is calculated to be about 0.01

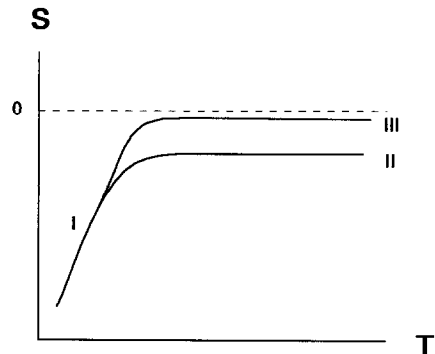


FIG. 3. Schematic illustration of the Seebeck coefficient (S) vs temperature curve for the system $(\text{Gd}_{1-x}\text{Ca}_x)\text{MnO}_{2.98}$.

to 0.02 eV from Eqs. (4) and (5). This value is nearly equal to that of $\text{Na}_{0.33}\text{V}_2\text{O}_5$ (8). T_d is lower than T_t by about 150 to 200 K. Though the spin state of the Mn^{3+} ion changes completely ($0.6 \leq x < 0.8$) or partially ($0.8 \leq x \leq 0.95$) at T_t , there is no remarkable change in S . In the range $0.8 \leq x \leq 0.95$, both low-spin Mn^{3+} (the semiconductive part) and high-spin Mn^{3+} ions (the metallic part) coexist above T_t . S of the metallic part follows curve III and that of the semiconductive part follows curve II. In general, the absolute value of S for the semiconductive part is larger than that for the metallic part. So, the observed S follows curves $\text{I} \rightarrow \text{II}$. On the other hand, in the range $0.6 \leq x < 0.8$, the low-spin state of Mn^{3+} ion (the semiconductive part) doesn't exist above T_t and S follows curves $\text{I} \rightarrow \text{II} \rightarrow \text{III}$. There is no remarkable change in S near T_t . We consider that curve II is nearly equal to curve III and S monotonously changes at T_t .

It is concluded that the electrical conductivity of $(\text{Gd}_{1-x}\text{Ca}_x)\text{MnO}_{2.98}$ follows Mott's $T^{-1/4}$ law at low temperature and S exponentially changes. With increasing temperature, the mechanism of the hopping conductivity changes and S is temperature-independent.

Above T_t , the spin state of Mn^{3+} completely or partially changes. In the range $0.8 \leq x \leq 0.95$, the spin state of Mn^{3+} is both low and high. S is temperature-independent and can be explained by the hopping model. On the other hand, in the range $0.6 \leq x < 0.8$, the spin state of the Mn^{3+} ion changes from low to high. Monotonous changes of S correspond to the change from semiconductor to metal.

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