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LARGE NEGATIVE THERMOPOWER IN ELECTRON-DOPED MANGANITES*

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New perovskites containing low concentration of Mn^{3+} (e_g^1) Jahn–Teller cations in a Mn^{4+} (e_g^0) cation matrix are synthesized. Theses manganites are metallic at room temperature ($\rho \sim 10^{-2}\Omega$cm) for small concentration of dopants ($y \leq 8\%$). Remarkably the samples exhibit large negative thermopower values at room temperature ($-S > 100\mu\mathrm{V}\cdot\mathrm{K}^{-1}$), which increases with increasing temperature. Therefore these materials are good candidates for n-leg parts of thermoelectric devices for the conversion of heat to electricity. In order to explain this interesting behavior, a new theoretical framework taking correlation effects and realistic electronic configurations into account, is introduced. It allows for determining the temperature and charge-carrier density dependences of the thermopower. The results are compared to the observed experimental values of $CaMn_{1-x}M_xO_3$, with M=Ru, Mo, which exhibit two different background states.

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1. Introduction

Metal transition oxides exhibit various kinds of spectacular physical properties such as high T_c superconductivity in cuprates and colossal magneto-resistance in manganites. More recently, Terasaki *et al.* [1] have shown that the $NaCo_2O_4$ cobaltite exhibits a high figure of merit Z and since then the research for new metallic oxides with large S values to be used for applications to convert heat to energy has become an important topic. For instance good characteristics (large S and low ρ) have been obtained for $Sr_{1-x}La_xTiO_3$ titanates [2] and the fabrication of an all-oxide thermoelectric power generator based on a "misfit cobaltite" and a perovskite manganite

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has been very recently reported [3]. The latter consists of A site doped oxides $Ca_{1-x}Ln_xMnO_3$ which have large absolute value of S at room temperature [4]. Since their S value is increasingly negative with increasing temperature, these oxides are interesting as n-leg for a thermoelectric device in air at high temperature. In this paper, we compare the resistivity and the thermopower results between lightly doped $CaMn_{1-x}Ru_xO_3$ and $CaMn_{1-x}Mo_xO_3$, where the substitution on the B site of Mn^{4+} by higher valency cations is expected to turn the insulating parent compound into conducting ones, and we discuss the origin of the differences between both series. We then turn to a simple description of the temperature dependence of S which is incorporating the details of a microscopic Hamiltonian.

2. Results

Here we report about the electrical and thermal transport coefficients of two series of compounds, derived from the insulating perovskite $CaMnO_3$, namely $CaMn_{1-x}M_xO_3$ with M=Ru, Mo, for small x. These ceramic samples were synthesized in the form of bars at 1400°C in air according to the procedure detailed in Ref. [5].

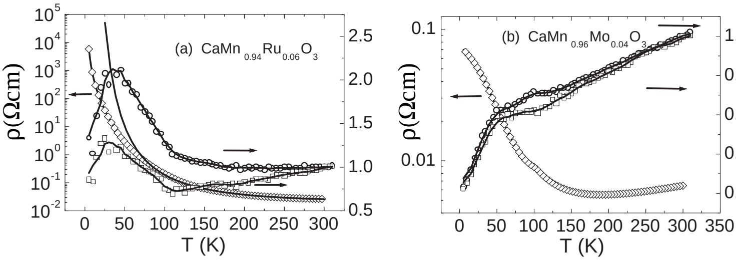

Fig. 1. (a) Resistivity (diamonds, left axis) and small polaron fit (full curve, left axis), thermopower (circles, right axis) and thermal conductivity (squares, right axis) as a function of temperature for $CaMn_{0.94}Ru_{0.06}O_3$. The latter two are normalized to their room temperature value ($S(300\text{K}) = -140\mu$ V/K, $\kappa(300\text{K}) =$ 5.2W/m/K). (b) Resistivity (diamonds, left axis), thermopower (circles, right axis) and thermal conductivity (squares, right axis) as a function of temperature for $CaMn_{0.96}Mo_{0.04}O_3$. The latter two are normalized to their room temperature value ($S(300\text{K}) = -104\mu\text{V/K}$, $\kappa(300\text{K}) = 3.6\text{W/m/K}$).

Taking as an example $CaMn_{0.94}Ru_{0.06}O_3$, its resistivity (ρ), thermopower (S) and thermal conductivity (κ) are shown on Fig. 1 (a). At "high" temperature ($T > 130\text{K}$), ρ is following a small polaron behavior ($\rho(T) \simeq AT \exp(T_0/T)$ [6]) with $T_0 \simeq 460\text{K}$ and $A \simeq 2 \cdot 10^{-5}\Omega\text{cm/K}$. At lower temperature a magnetic transition occurs, and the data deviate from this behavior before the system turns insulating at low temperature. Still, $\rho(T)$ is a smooth curve, and the magnetic transition only appears as a deviation to the small polaron behavior. Its influence on κ is more pronounced. Indeed it is noticeably suppressed around $T = 130$K, as compared to its value at both room temperature and $T = 40$K, where it shows a marked peak. This peak is more pronounced in the thermopower. The latter is quite large at room temperature ($S(300\text{K}) \simeq -140\mu\text{V/K}$), and is enhanced by over a factor two at 40K. Here we note that S is getting only weakly T-dependent above 200K, while ρ decreases. This results into a figure of merit which increases with temperature, making these systems interesting for high T applications. The behavior of the Mo substituted samples is rather different, even though a magnetic transition occurs at $T \simeq 100$K. First of all it does not display an insulating behavior at low temperature, as shown in Fig. 1 (b) for $\text{CaMn}_{0.96}\text{Mo}_{0.04}\text{O}_3$. Second, the magnetic transition is reflected in the resistivity curve as a shoulder around $T = 100$K. Third the high temperature resistivity is not as well described by the small polaron model as the Ru substituted samples are. Fourth the ratio S/κ is only weakly T-dependent, except for the domain around the magnetic transition. All these differences may appear rather amazing since both systems are made “metallic” by small cationic substitution on the B site of the same perovskite. Some of these differences may be accounted for by noticing that the non-magnetic Mo^{6+} ions only acts as donors to the e_g bands, while the Ru ions participate to the formation of broader e_g bands on top of coupling magnetically to the Mn ions. Moreover the T-dependence of S can be understood in a unified picture following from the dispersion relations particular to e_g bands. Following Mahan [7], we write

$$S(T) = \frac{k_\text{B}}{|e|}\frac{\mu(T) - E_0}{k_\text{B}T} \ . \tag{1}$$

We determine the chemical potential μ from a microscopic Hamiltonian which includes the two Mn e_g, and O $2p$, energy levels located at ε_d and ε_p, and the corresponding overlap integrals. Here we use $\varepsilon_d - \varepsilon_p = 2$ eV, which is typical for these oxides. In Eq. (1) E_0 is understood as a parameter accounting for the ratio of the energy current particle current correlation function to the particle current auto-correlation function. It is determined by demanding that the calculated S reproduces the measured one at 300K. The result of carrying out this program is shown in Fig. 2. The experimental data are reproduced by Eq. (1) over the entire temperature range above the magnetic transition, and even partly below. As we can use a T-independent E_0 in this range, we conclude that the magnetic transitions have little influence on S in these compounds. Its origin is therefore non-magnetic, and might be attributed to strong correlation effects, as in the high temperature analysis of Oudovenko and Kotliar [8]. We also note that the band width W is smaller for the Mo case, as for the Ru case, in agreement with the above discussion.

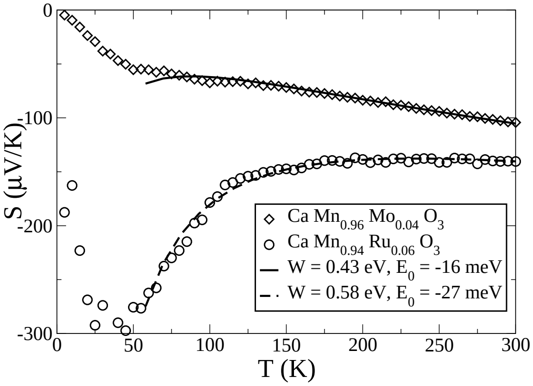

Fig. 2. Temperature dependence of the thermopower for $\mathrm{CaMn_{0.96}Mo_{0.04}O_3}$ (diamonds), $\mathrm{CaMn_{0.94}Ru_{0.06}O_3}$ (circles), and numerical results.

3. Summary

In summary, we synthesized two sets of samples, $\mathrm{CaMn}_{1-x}\mathrm{Ru}_x\mathrm{O}_3$ and $\mathrm{CaMn}_{1-x}\mathrm{Mo}_x\mathrm{O}_3$. With large thermopower, low thermal conductivity and small resistivity, these materials are good candidates for applications as n-leg of thermopower generators to be used at high temperatures ($T \gg 300$K). We also worked out a model for the temperature dependence of the Seebeck coefficient which accounts for the experimental data.

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