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Correlation of the size effect with the thermoelectric power for the Pr-based manganites $Pr_{0.7}Ca_{0.3-x}Sr_xMnO_3$

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The thermoelectric power (TEP) S versus temperature has been investigated for the manganite $Pr_{0.7}Ca_{0.3-x}Sr_xMnO_3$ series. Although these materials exhibit the same hole concentration considering their Mn valency of 3.3, their $S(T)$ curves are dramatically affected when x varies from 0 to 0.3, i.e., when the mean size of the interpolated cation increases. Particularly the $S_{290\ \mathrm{K}}$ values go from positive to negative when x increases. The remarkable feature is that TEP data for samples which exhibit colossal magnetoresistive (CMR) properties are found to be similar and can be well described by the paramagnetic (P)-antiferromagnetic (AF) and AF-ferromagnetic (F) transitions which exist in these samples. On the other hand, for the samples with higher x values, the CMR effect is smaller and the $S(T)$ curves change shape. Clearly, the electronic properties of these materials are very sensitive to the atomic orbitals overlapping which can be varied via cationic size variations as demonstrated by the present TEP measurements. Moreover, the signatures of both P→AF and AF→F transitions on the TEP curves seem to be a good indicator to detect samples with CMR properties. [S0163-1829(96)04141-0]

INTRODUCTION

The recent discovery of a negative colossal magnetoresistance (CMR) in manganese perovskite clearly demonstrates that these phases must be revised to explain their exceptional properties.[1] These materials were studied for their remarkable magnetic structures which are very sensitive to the y value in the general formula $L_{1-y}A_yMnO_3$ $(0 \leqslant y \leqslant 1)$ and particularly in the $Pr_{1-y}A_yMnO_3$ phases.[2–4] A dramatic change of the electrical resistivity, culminating at temperature $T_{\max}$, separate a semiconducting paramagnetic state (SP), existing for $T > T_{\max}$, from a metallic-ferromagnetic (MF) state stabilized for $T < T_{\max}$.[5,6] In fact $T_{\max}$ is very sensitive to the average size and mean valency of the large cation and the temperature dependence of electrical resistivity is strongly modified by application of a magnetic field; the M-S transition broadens, $T_{\max}$ increases and electrical resistivity decreases. Moreover the phase diagram was found to be complicated for x approaching to 0.5, since an antiferromagnetic transition is observed at $T_N < T_{\max}$. This temperature separates the F phase $(T_N \leqslant T \leqslant T_{\max})$ and the antiferromagnetic phase for $T < T_N$.[14] This composition has been recently reinvestigated by Tomioka *et al.*[7] and a strong magnetoresistance effect $R_{B=0}/R_{B=7\ \mathrm{T}}$ of 100 has been evidenced at 5 K.

However, larger CMR effects have recently been evidenced in $Pr_{0.7}A_{0.3}MnO_3$ series with $R_{B=0}/R_{B=5\ \mathrm{T}}$ ratio up to 10^{11}.[8,9] Moreover, these studies have shown the dramatic effect of the size of the interpolated cation both on the $T_{\max}$ and the CMR effect. For instance, in the $Pr_{0.7}Ca_{0.3-x}Sr_xMnO_3$ series, $T_{\max}$ was found to be shifted from 88 K for $x=0.05$ to 230 K for $x=0.20$, the $x=0.05$ sample exhibiting a CMR effect ($R_{B=0}/R_{B=5\ \mathrm{T}}=2\ 10^5$ at 88 K).[5]

The variations of resistivity at $T_{\max}$ from SP phase to MF one make recalls to probe more deeply the electronic properties of these materials. One of the most sensitive experiments which probes the carriers in the system is the thermopower measurement.

Hence we present in this study a systematic thermoelectric power characterization for $Pr_{1-y}A_yMnO_3$ samples (A =Ca, Sr, and Ba) for which resistive, magnetic, and magnetoresistive properties have been extensively studied. Both the size and charge effects of the interpolated cations are compared.

EXPERIMENTAL

The samples were prepared and structurally characterized according to Ref. 5. Magnetic data were registered with a superconducting quantum interference device magnetometer and were also obtained from powder neutron-diffraction studies.[11]

Resistive and magnetoresistive studies were carried out with a four-probe technique in the 5 K$\leqslant T \leqslant$300 K range with magnetic field ranging from 0 to 5 T.

A dynamic two-point method was employed for the measurement of the thermoelectric power. The samples were attached with silver paint between two small blocks with adjustable temperature gradient which was monitored using Pt sensors. The assembly was placed in a closed-cycle He cryostat and the measurements were carried out while the temperature of the assembly was slowly increased from 15 to 300 K with the rate of 0.5 K min^{-1}. A variable temperature gradient up to 0.5 K between the copper electrodes was created; the thermoelectric voltage (ΔV) and temperature gradient (ΔT) were measured. The thermoelectric power (S) was then calculated from the slope of $(\Delta V)=f(\Delta T)$.

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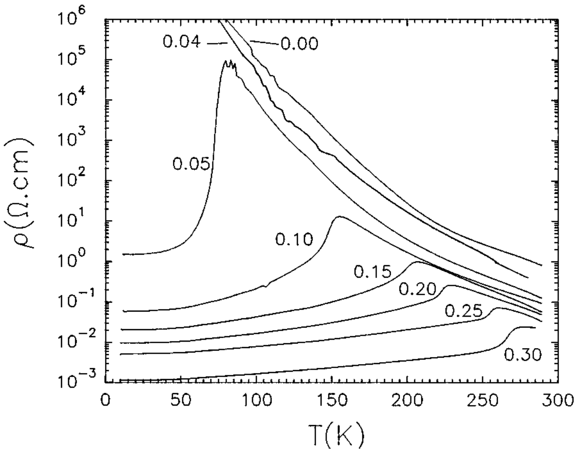

FIG. 1. T dependence of the resistivity for samples of the $Pr_{0.7}Ca_{0.3-x}Sr_xMnO_3$ series; x values are labeled on the graph. (10^6 Ω cm corresponds to the experimental limit.)

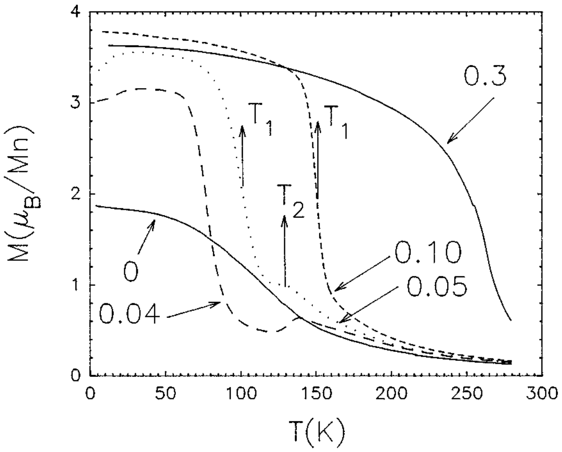

FIG. 2. T dependence of the magnetization for the $Pr_{0.7}Ca_{0.3-x}Sr_xMnO_3$ sample; T_1 and T_2 are labeled on the graph.

RESULTS AND DISCUSSION

The $Pr_{0.7}Ca_{0.3-x}Sr_xMnO_3$ series was investigated in order to vary the mean size of the interpolated cation (Sr^{2+} is larger than Ca^{2+}), while keeping the nominal Mn^{3+}/Mn^{4+} ratio unchanged. The constant mixed valence of manganese in the $Pr_{0.7}Ca_{0.3-x}Sr_xMnO_3$ series was confirmed in our recent studies[11] when using the energy-dispersive spectrometry and neutron-diffraction analysis both nominal cationic compositions and oxygen ''O_3'' stoichiometry were proved.

In the $0 \leqslant x \leqslant 0.04$ range, the resistivity curves registered in earth magnetic field exhibit a semiconducting behavior in the whole studied temperature range (Fig. 1). The experimental setup limits the resistivity measurements to around 10^6 Ω cm for the samples. Nevertheless, even at low temperature (10 K) no measurable resistivities were obtained for these samples. For higher x concentrations ($x > 0.04$) all the curves are characterized by a peak at T_{max} which separates a semiconductinglike behavior for $T > T_{max}$ and a semimetallic state for $T \ll T_{max}$ (Fig. 1). Further increase of the Sr content (x), i.e., of the size of the interpolated cation, has the following consequences:

(i) The ratio $R_{(T_{max})}/R_{(10\ K)}$ decreases when the A cation size increases.

(ii) T_{max} shifts to higher temperatures.

(iii) The absolute value of electrical resistivity at 290 K decreases.

This dramatic change of conducting behavior is in fact related to the magnetic properties of the samples[11] which present a systematic transition from a pure ferromagnetic or mixed ferro-antiferromagnetic state when T is increased to a paramagnetic state, the corresponding transition temperature T_1 being close to T_{max} (Fig. 2). The correlation between magnetism and electrical properties was recently studied for $Pr_{0.7}Ca_{0.3-x}Sr_xMnO_2$ ($x = 0.05$, 0.1);[12] furthermore, neutron data refinements performed on both $x = 0.05$ and $x = 0.1$ samples have demonstrated that, in zero magnetic field, the former composition exhibits two magnetic transitions: ferromagnetic (F) ($T < T_1$), antiferromagnetic (AF) ($T_1 < T < T_2$) and then paramagnetic (P) ($T > T_2$) (see Fig. 2), and the latter $x = 0.10$ sample only one F-P transition.[11] In both samples the apparition of ferromagnetism at $T < T_1$ corresponds to the observed decrease of electrical resistivity.

Moreover the resistivity study revealed that two characteristic groups in the $Pr_{0.7}Ca_{0.3-x}Sr_xMnO_3$ series exist (Fig. 1):

(i) Samples with activated electrical resistivity down to 75 K ($0.0 \leqslant x \leqslant 0.04$); below this temperature resistances are too high to be measured.

(ii) Samples which exhibit SP-MF transition without external magnetic field ($x \leqslant 0.05$).

For the first series of samples ($x \leqslant 0.04$) CMR effects are observed [up to 10^{11} at 30 K for $B = 5$ T and $x = 0.04$ (Refs. 8 and 9)]. In the second series, the samples exhibit a peak at T_{max} with culminating CMR close to this temperature. The CMR effect decreases when T is shifted from T_{max} to both low and high temperatures.[5,6]

The temperature dependences of thermoelectric power (TEP) for the $Pr_{0.7}Ca_{0.3-x}Sr_xMnO_3$ series are given in Fig. 3. The high sensitivity of the TEP to the composition variation is strongly pronounced. Two families of samples separated by the borderline composition $Pr_{0.7}Ca_{0.2}Sr_{0.1}MnO_3$ could be

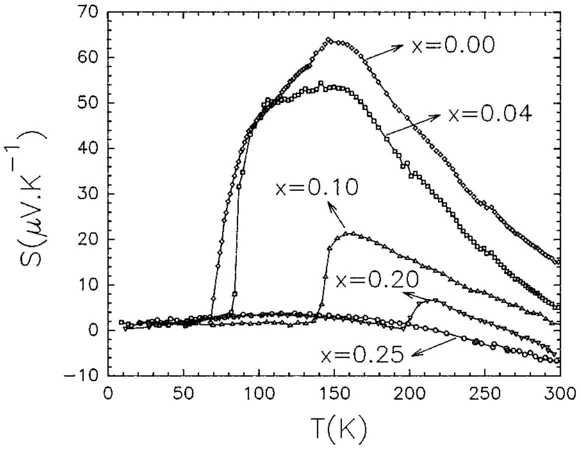

FIG. 3. T dependence of the thermopower S for different x values chosen in the series $Pr_{0.7}Ca_{0.3-x}Sr_xMnO_3$.

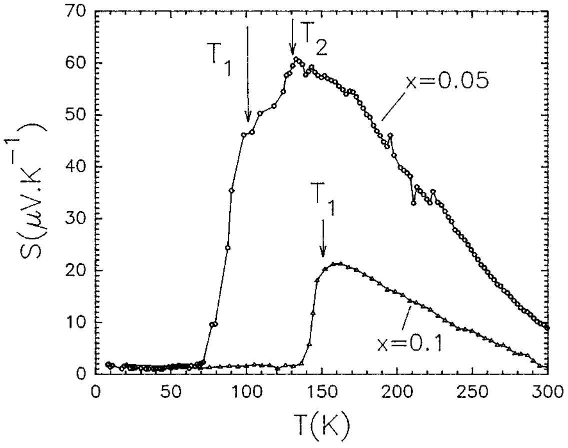

FIG. 4. $S(T)$ curves of $Pr_{0.7}Ca_{0.25}Sr_{0.05}MnO_3$ ($x=0.05$) and $Pr_{0.7}Ca_{0.2}Sr_{0.1}MnO_3$ ($x=0.1$); T_1 and T_2 are extracted from the $M(T)$ curves.

distinguished. The samples with $0 \leqslant x < 0.1$ have a similar behavior. TEP increases from values close to 10 $\mu V\,K^{-1}$ at 290 K with decreasing temperature and after reaching a value of 60 $\mu V\,K^{-1}$ at $\approx$150 K (close to T_2 which is defined from the $M(T)$ curves as the P-AF transition) then smoothly decreases and finally falls down from $T \approx T_1$ to reach nearly zero at about 70 K [T_1 corresponds to the AF-F transition on the $M(T)$ curves]. The second family ($0.1 \leqslant x \leqslant 0.20$) is represented by a sharp drop of TEP at temperatures corresponding to the P-F transition at $T \approx T_1$ (or T_{max}). Both kinds of TEP behaviors are illustrated in Fig. 4 for $x=0.05$ and $x=0.1$ where the characteristic temperatures T_1 and T_2 from magnetization data are also reported. With increasing x ($0.20 \leqslant x \leqslant 0.30$) the transitions on the $S(T)$ curves (Fig. 3) becomes less pronounced and the shape of the curves evolves as x increases from strongly T dependent to less dependent [see for instance the $S(T)$ curve of the $x=0.25$ sample].

Moreover the sign of the TEP at room temperature changes. This is clearly evidenced in Fig. 5(a) where the $S_{290\ K}$ values are reported as a function of x. Thus, this TEP change of sign at room temperature when the cationic size increases for samples which exhibit the same Mn valency (neutron structural refinements confirm the O_3 stoichiometry[11]) cannot be attributed to a change of carriers from electron to holes. Such a sign upturn was also observable for hole-doped superconducting cuprates in the function of doping[10] and is still a matter of debate: Kubo *et al.* have shown that TEP values at room temperature are very sensitive to the band structure of these materials.[13] The present sensitivity of the TEP data for $Pr_{0.7}Ca_{0.3-x}Sr_xMnO_3$ when x is varied suggests that the strong electronic modifications induced by the size effect are correlated to the overlapping of the atomic Mn-O orbitals. A possibility of interpretation is an evolution of the Jahn–Teller effect which is larger for the smaller x values (smaller ionic radii of the interpolated cation).[2–4] The room-temperature resistivity is also smaller for large x values. On the other hand, it cannot be ruled out that the effects of the Coulombian localization, which are often invoked for the CMR properties,[7,12] also play a role in the TEP values.

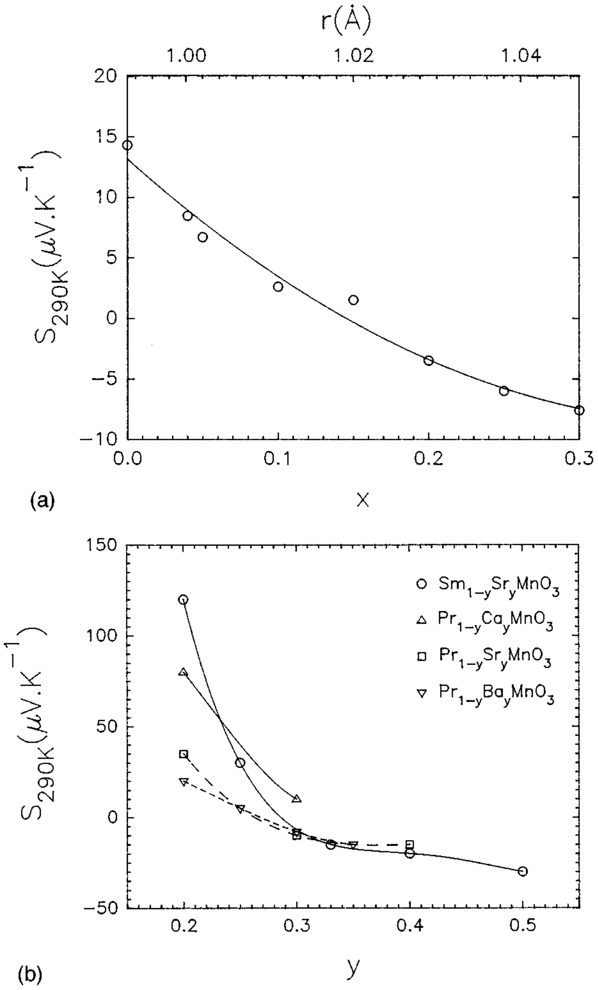

FIG. 5. (a) x dependence (bottom x axis) or ionic radius of the interpolated cation (r) dependence (top x axis) of $S_{290\ K}$ for the $Pr_{0.7}Ca_{0.3-x}Sr_xMnO_3$; (the line is just a guide to the eye). (b) y dependence of $S_{290\ K}$ for the series $Pr_{1-y}A_yMnO_3$ ($A=Ca^{2+}$, Sr^{2+}, Ba^{2+}) and $Sm_{1-y}Sr_yMnO_3$ series (lines are guides to the eye).

These results also show the difficulties to interpret CMR and TEP data in a series of materials where not only the size effect is varied but also the formal Mn valency. To illustrate this point, we have performed systematic TEP measurements for three $Pr_{1-y}A_yMnO_3$ series ($A=Ca^{2+},Sr^{2+},Ba^{2+}$), where A^{2+} ionic size increases from Ca^{2+} to Sr^{2+} and then to Ba^{2+} [Fig. 5(b)]. These results are also compared to those obtained for another series with a different lanthanide cation, $Sm_{1-y}Sr_yMnO_3$ for which large CMR effects have also been reported.[14] For each A cation $S_{290\ K}$ depends strongly on the valence: it decreases as the valence increases and the change of sign has no special meaning. This result was also previously observed for superconducting copper oxides which exhibit large resistivity variations at the superconducting transition (T_c). For these latter materials, a systematic variation of the TEP values at room temperature has been evidenced.[10] The measurements have shown that, when by means of chemical substitutions the doping is varied, the highest T_c—or optimal doping—for any superconducting phase correlates with a $S_{290\ K}$ value (at 290 K) close to 0. Further a systematic shift of $S_{290\ K}$ with the doping was evidenced;

''underdoped'' materials exhibit positive $S_{290\ \mathrm{K}}$ values which increase when doping decreases and ''overdoped'' materials negative $S_{290\ \mathrm{K}}$ values which decrease when doping increases. According to the structural and bonding similarities between these mixed-valent copper and manganese oxides, such a discrepancy between the TEP decrease and the increase of the formal hole content may be interpreted as in the case of the cuprates by the peculiar band structure close to the Fermi level.[13] On the other hand, if one compares the different $\mathrm{Pr}_{1-y}A_y\mathrm{MnO}_3$ series it appears that the TEP is very sensitive to the interpolated cation size and that this effect increases when y decreases: for $y=0.3$, one can see in Fig. 5(b) that the effect on $S_{290\ \mathrm{K}}$ is not very large but on the opposite for $y=0.2$ the size effect on the $S_{290\ \mathrm{K}}$ values is much larger than the valency effect on the $\mathrm{Pr}_{1-y}\mathrm{Ba}_y\mathrm{MnO}_3$ series. In this latter series, neutron data have evidenced that the cell parameters are quite insensitive to y, i.e., the ionic size of the interpolated cation $\mathrm{Pr}_{1-y}\mathrm{Ba}_y$ variation is compensated by the $\mathrm{Mn}^{3+}_{1-y}\mathrm{Mn}^{4+}_{y}$ mixed valence.[3] For this reason, the Ba^{2+} substitution can be considered as the ''pure'' valence dependence of the TEP. However, the comparison between the effects of Ba^{2+}, Ca^{2+}, and Sr^{2+} evidences the role of the size effect as presented in Fig. 5(a) for the $\mathrm{Pr}_{0.7}\mathrm{Ca}_{0.3-x}\mathrm{Sr}_x\mathrm{MnO}_3$ series.

CONCLUSION

In the present study the temperature (T) dependence of the thermopower (S) has been investigated for the $L_{1-y}A_y\mathrm{MnO}_3$ series of samples in which both size of the interpolated cation and valence have been varied. For a constant valence ($y=0.3$), corresponding to the formula $\mathrm{Pr}_{0.7}\mathrm{Ca}_{0.3-x}\mathrm{Sr}_x\mathrm{MnO}_3$, it has been shown that $S_{290\ \mathrm{K}}$ values decrease from $+15$ to $-7\ \mu\mathrm{V\ K}^{-1}$ when x increases from 0 to 0.3 and correlatively the $S(T)$ curves exhibit signatures of both P→AF and AF→F transitions for smallest x values. In that sense, thermopower measurements seem to be a good indicator to detect samples with CMR properties. Moreover, the comparison of different $L_{1-y}A_y\mathrm{MnO}_3$ series where the valence is varied indicates that for the smallest y values this size effect becomes even larger varying from $+40\ \mu\mathrm{V\ K}^{-1}$ for $\mathrm{Pr}_{0.8}\mathrm{Sr}_{0.2}\mathrm{MnO}_3$ to $+80\ \mu\mathrm{V\ K}^{-1}$ for $\mathrm{Pr}_{0.8}\mathrm{Ca}_{0.2}\mathrm{MnO}_3$.

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[1] R. von Helmot, J. Wecker, B. Holzapfel, L. Schultz, and K. Samwer, Phys. Rev. Lett. **71**, 2331 (1993).

[2] Z. Jirak, S. Krupicka, Z. Simsa, M. Dlouha, and S. Vratislav, J. Magn. Magn. Mater. **53**, 153 (1985).

[3] Z. Jirak, E. Pollert, A. F. Andersen, J. C. Grenier, and P. Hagenmuller, Eur. J. Solid State Inorg. Chem. **27**, 421 (1990).

[4] K. Knizek, Z. Jirak, E. Pollert, F. Zounova, and S. Vratislav, J. Solid State Chem. **100**, 292 (1992).

[5] B. Raveau, A. Maignan, and V. Caignaert, J. Solid State Chem. **117**, 424 (1995).

[6] A. Maignan, Ch. Simon, V. Caignaert, and B. Raveau, Z. Phys. B **99**, 305 (1995).

[7] Y. Tomioka, A. Asamitsu, Y. Moritomo, H. Kuwahara, and Y. Yokura, Phys. Rev. Lett. **74**, 5108 (1995).

[8] A. Maignan, Ch. Simon, V. Caignaert, and B. Raveau, Solid State Commun. **96**, 623 (1995).

[9] A. Maignan, Ch. Simon, V. Caignaert, and B. Raveau, C.R. Acad. Sci. **321** (**IIb**), 297 (1995).

[10] S. D. Obertelli, J. R. Cooper, and J. L. Tallon, Phys. Rev. B **46**, 14 928 (1992).

[11] V. Caignaert, E. Suard, A. Maignan, Ch. Simon, and B. Raveau, J. Magn. Magn. Mater. **152**, 5 (1995).

[12] A. Maignan, Ch. Simon, V. Caignaert, and B. Raveau, J. Magn. Magn. Mater. **153**, 260 (1996).

[13] Y. Kubo, Phys. Rev. B **50**, 3181 (1994).

[14] V. Caignaert, A. Maignan, and B. Raveau, Solid State Commun. **95**, 357 (1995).