Observation of the thermal hysteresis of thermoelectric power in $Pr_{0.5}(Sr, Ca)_{0.5}MnO_3$

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Abstract. The strong thermal hysteresis of thermoelectric power (TEP) in $Pr_{0.5}(Sr, Ca)_{0.5}MnO_3$ is observed. A simple estimation shows that the electrostatic energy between Mn^{3+}/Mn^{4+} alone cannot account for the large shift of T_{co} with changing A size. Based on our experimental evidence, we attribute the distinct features exhibited in the thermal hysteresis to the manifestation of the underlying competition between the delocalization and localization effects assisted respectively by the double exchange interaction and the charge ordering. The observed features include the following: (1) the A-size effect can depress T_{co} by as much as 70 K for $Pr_{0.5}Sr_{0.5-x}Ca_xMnO_3$; (2) large thermal hysteresis of resistivity and TEP are exhibited in $Pr_{0.5}Sr_{0.5-x}Ca_xMnO_3$; (3) for $x = 0.3$ and 0.4, the thermal hysteresis is larger than those of $x = 0.1$ and 0.5 and (4) magnetic field induces a large shift in T_{co}.

1. Introduction

The perovskite structure of $Ln_{1-x}A_xMnO_3$ (Ln = La, Pr, Nd, etc, A = Ca, Sr, Ba) shows long-range real space ordering when the Mn^{3+}/Mn^{4+} forms a commensurate state. The formation of the charge ordering state is believed to be in conjunction with the suppression of the kinetic energy of carriers due to the mutual Coulomb interaction between carriers [1]. For samples with $Mn^{3+}/Mn^{4+} = 1$, the interplay of ferromagnetism, antiferromagnetism, charge ordering and the lattice effect gives very intriguing phenomena. The reported results for $Pr_{0.5}Sr_{0.5-x}Ca_xMnO_3$ are summarized as the following.

(1) For $Pr_{0.5}Sr_{0.5}MnO_3$, a ferromagnetic state appears at $T_c = 250$ K, while for $Pr_{0.5}Ca_{0.5}MnO_3$, no ferromagnetic state is observed [1, 2]. For intermediate x, a coexistence of ferromagnetic/metallic and antiferromagnetic/insulator state was observed [3].

(2) $Pr_{0.5}Sr_{0.5}MnO_3$ shows a coincidence of resistivity jump and the appearance of the A-type antiferromagnetic state at $T_N = 150$ K. But for $x > 0.4$, the antiferromagnetic state becomes CE type and T_{co} increases with increasing x and reaches its maximum at $T_{co} = 250$ K for $x = 0.5$. On the other hand, T_N remains relatively unchanged ($T_N \sim 170 \pm 20$ K) with respective to different x [3, 4].

(3) Resistivity, susceptibility and lattice parameter measurements show pronounced thermal hysteresis [1, 3, 5, 6].

(4) The charge ordering state collapses under a strong magnetic field [1].

It is important to note that the charge ordering state exists not only in the system with $Mn^{3+}/Mn^{4+} = 1$ but also in any system where the Mn^{3+}/Mn^{4+} ratio forms a commensurate state. In fact, Hwang and Cheong have shown that the charge ordering state forms whenever the Mn^{3+}/Mn^{4+} ratio is equal to $N/8$ ($N = 1, 3, 4, 5$ and 7) [7]. It was demonstrated that the collapsing of the charge ordering for $Pr_{0.5}Sr_{0.5}MnO_3$ requires a magnetic field larger than 7 T [1], whereas, for $La_{7/8}Ca_{1/8}MnO_3$, a small field ~ 90 Oe was high enough to suppress the charge ordering [7]. When $Mn^{3+}/Mn^{4+} = 1$, the charge ordering state is expected to be the most robust one since the Coulomb interaction between the Mn^{3+}–Mn^{4+} sites is expected to be the strongest.

The thermoelectric power (TEP) technique enables us to detect the electronic structure of a metal or an insulator. It is especially powerful for probing the system with an insulator–metal transition. The idea of investigating the system of $Pr_{0.5}Sr_{0.5-x}Ca_xMnO_3$ is to study the A-size effect without changing the Mn^{3+}/Mn^{4+} ratio. By varying the A size (the mean ionic radius of '$Sr_{0.5-x}Ca_x$'), we are able to study the size effect on T_c and T_{co}.

2. Experiment

Samples of $Pr_{0.5}Sr_{0.5-x}Ca_xMnO_3$ were synthesized by the solid state reaction of high purity powders of Pr_6O_{11}, $SrCO_3$, $CaCO_3$, Cr_2O_3 and $MnCO_3$. The Pr_6O_{11} powders were first dried at $950\,°C$ for 3 hours. Powders were well ground, pelletized and heated at $1400\,°C$ for 16 hours at least three times. All samples exhibited single phases based on the x-ray diffraction (XRD) patterns. The standard four-probe method was used to obtain the resistivity. The absolute TEP of the sample was obtained by a dc method and was calibrated against a Pb standard. A Cu/constantan thermocouple was used to detect the temperature gradient which was kept in the range of 0.8–1.2 K. The same samples were used for resistivity and TEP measurements. Both resistivity and TEP measurements were carried out in a closed cycle cryostat with a cold finger in vacuum. Since the non-equilibrium effect often gives pseudo-thermal-hysteresis signals, each TEP measurement point was stabilized for 5, 10 and 25 min, respectively to check the measurement. It should be emphasized that the thermal hysteresis has been observed in resistivity, susceptibility and lattice parameter measurements [1, 3, 5, 6]. Furthermore, experiments on both single crystals and polycrystallines give similar thermal hysteresis results [1, 3]. Hence we believe the observed thermal hysteresis in our samples is a real intrinsic property of the samples, and it should not be mistaken as a polycrystalline feature.

3. Results and discussion

Figure 1 shows the magnetization data (ZFC) for $Pr_{0.5}Sr_{0.5-x}Ca_xMnO_3$. We define the first inflection ($d^2M/dT^2 = 0$) of magnetization as T_c, and define the second inflections as the charge ordering temperature (T_{co}). The critical temperatures obtained by different measurements are shown in table 1 for comparison. For $Pr_{0.5}Sr_{0.1}Ca_{0.4}MnO_3$ and $Pr_{0.5}Ca_{0.5}MnO_3$, the magnetization is relatively small. This is consistent with an earlier report that a ferromagnetic state does not exist in $Pr_{0.5}Ca_{0.5}MnO_3$ [8]. Notably, increasing the A size changes the T_{co} by almost 70 K (from ~ 240 K for $x = 0.5$ to ~ 170 K for $x = 0.1$).

If the charge ordering state is simply the electrostatic interaction between Mn^{3+} and Mn^{4+}, the only reason for the shift of T_{co} should be the lattice variation with different x. However, in the following paragraph, we will provide a simple estimation to show that the large shift of T_{co} cannot be attributed to the lattice variation if we simply take the electrostatic energy into consideration.
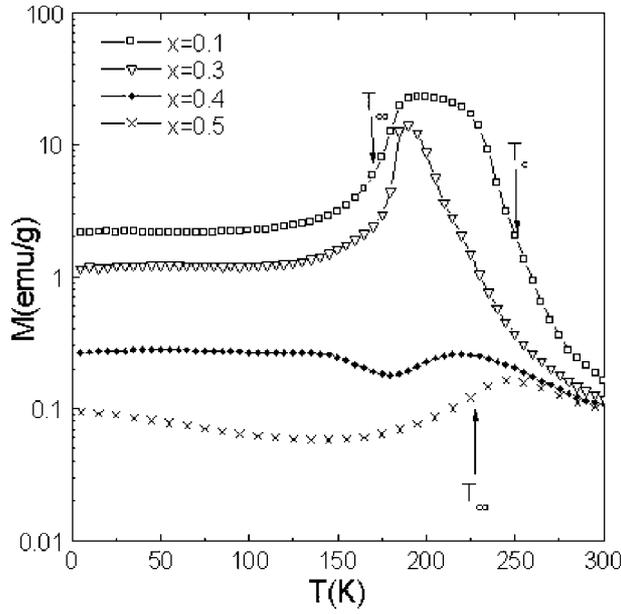
Figure 1. Magnetization data for Pr$_{0.5}$Sr$_{0.5-x}$Ca$_x$MnO$_3$. The T_c and T_{co} for $x = 0.1$ and 0.5 are specified by the arrows in the figure.

Table 1. The T_c and T_{co} values obtained by the magnetization and the TEP data in warming processes are listed for comparison.

x	T_c (by M–T) (K)	T_c (by TEP) (K)	T_{co} (by M–T) (K)	T_{co} (by TEP) (K)
0.1	250	250	170	170
0.2	235	240	175	175
0.3	230	210	180	180
0.4	—	—	200	195
0.5	—	—	230	240

The free energy F of the charge ordering state can be written as the general form:

$$F = U - TS \tag{1}$$

where U is the internal energy, T temperature and S entropy. For the charge ordering state, U should be determined mainly by the electrostatic energy of Mn^{3+} and Mn^{4+}. So U can be written as:

$$U = -\frac{e^2}{4\pi\varepsilon r}. \tag{2}$$

On the other hand, S is determined by the Boltzmann formula:

$$S = k\ln W \tag{3}$$

where k is the Boltzmann constant and W the configuration number. For ideal cases, $W \sim 10^0$ since they are in an 'ordered state'. Although different types of charge ordering or charge stripes have been observed [3, 4, 9], their contribution to S should be of the same order of magnitude. If we take $r \sim 4$ Å [10], and e is equal to the electron charge, the rough estimation for the free energy shows that the second term is just $\sim 10^{-4}$ of the first term in equation (1). Therefore, the free energy of the charge ordering state is mainly determined by the electrostatic

energy between Mn^{3+} and Mn^{4+}. Since T_{co} for $Pr_{0.5}Sr_{0.4}Ca_{0.1}MnO_3$ and $Pr_{0.5}Ca_{0.5}MnO_3$ are 170 and 240 K, respectively, the difference of free energy between them is:

$$\Delta F \approx \Delta U - \Delta T S \approx \Delta U. \tag{4}$$

Since we are discussing the electrostatic energy at two temperatures (170 K for $Pr_{0.5}Sr_{0.4}Ca_{0.1}MnO_3$ and 240 K for $Pr_{0.5}Ca_{0.5}MnO_3$), it is necessary to take into account the effect of the lattice variation Δr. Δr might result from a combination of the A-size effect, the temperature dependent lattice contraction and the structure transition at T_{co}. Assume $\Delta r/r = 10\%$ (from neutron diffraction data, $\Delta r/r$ is actually less than 10%, we take this value just for estimation) [10],

$$\Delta U = -\frac{e^2}{4\pi\varepsilon(r-\Delta r)} + \frac{e^2}{4\pi\varepsilon r} \simeq -\frac{e^2}{4\pi\varepsilon r}\frac{\Delta r}{r} \propto 240\text{ K} \times 10\% = 24\text{ K}.$$

So the change of the free energy due to the lattice variation is $\sim$24 K.

For $Pr_{0.5}Sr_{0.5-x}Ca_xMnO_3$, if there is no interaction competing with the charge ordering electrostatic energy, the charge ordering should have appeared at a small temperature window $\sim$(240$\pm$24) K for all x, where $\pm$24 K is due to lattice variation. The fact that T_{co} changes from 240 K for $x = 0.5$ to 170 K for $x = 0.1$ makes us believe that there must be another interaction competing with the charge ordering electrostatic interaction in $Pr_{0.5}Sr_{0.5-x}Ca_xMnO_3$. This interaction should be sufficiently strong to prevent the charge ordering state to appear at $\sim$240 K for $Pr_{0.5}Sr_{0.4}Ca_{0.1}MnO_3$. Since the ferromagnetic state appears at $\sim$250 K for $Pr_{0.5}Sr_{0.4}Ca_{0.1}MnO_3$, the ferromagnetic state must be competing with the charge ordering electrostatic energy.

Figure 2 displays the resistivity data for $Pr_{0.5}Sr_{0.5-x}Ca_xMnO_3$. Although the insulator–metal transition has been observed in single crystal $Pr_{0.5}Sr_{0.5}MnO_3$ [11], our data do not show such a result. We propose that it is because of the grain boundary effect which contributes additional resistance across the sample and thus smears out the small resistance change at T_c. Notably, there is a thermal hysteresis in resistivity for all compositions we have investigated. The resistivity for the warming curve is always larger than those of the cooling one. This behaviour has been taken as an indication of the first order transition at T_c and T_{co}.

Figure 3 exhibits the magnetic field effect on the resistivity. We simply show the effect on $x = 0.2$ for clarity. With increasing magnetic field, T_{co} shifts from 190 to 125 K. One would be surprised at the large shift of T_{co} if simply considering the electrostatic interaction alone. The simple relation $\mu_B H \sim k\Delta T_{co}$ is too small unless we take into account the effect from the double exchange interaction. Besides, the resistivity below T_{co} decreases with increasing magnetic field, indicating the emergence of the delocalization effect. The field-induced delocalization in the charge ordering region also supports our argument that it is the ferromagnetic delocalization effect that competes with the charge ordering interaction.

Figure 4 shows the TEP results obtained during the cooling process for $Pr_{0.5}Sr_{0.5-x}Ca_xMnO_3$. Although our resistivity data do not show the expected insulator–metal transition at T_c, the TEP result clearly shows a change of slope at T_c. This indicates that the TEP measurement is not so sensitive to the grain boundary effect. At certain temperatures, the changes of the slope are obvious and we can thus define T_c and T_{co} from the TEP data. The T_c and T_{co} values obtained from the TEP measurement are close to those obtained from the magnetization data as shown in table 1.

Since the TEP is a measure of the carrier energy, it reveals the nature of an insulator or a metal at different temperature ranges. It has been reported that $Pr_{0.5}Sr_{0.5}MnO_3$ first undergoes the insulator–metal transition at T_c and becomes insulator-like for $T < T_{co}$. But for
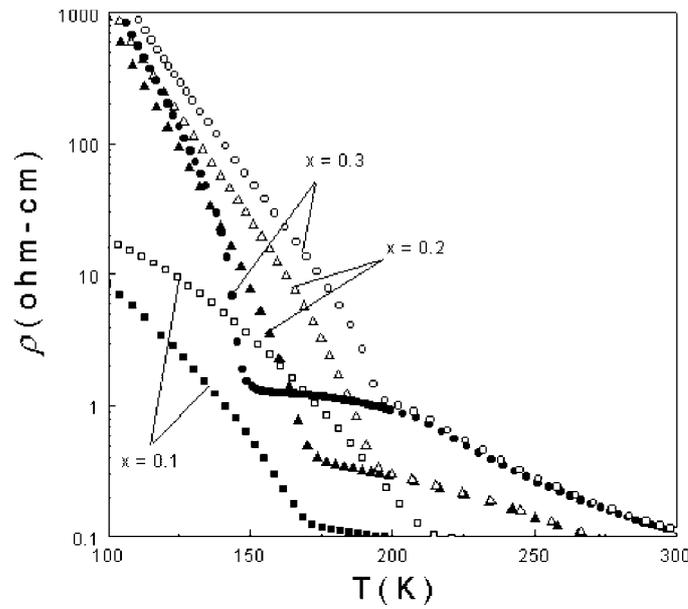
Figure 2. Resistivity (ρ) data for $Pr_{0.5}Sr_{0.5-x}Ca_xMnO_3$. Some of the resistivity data are not shown here for clarity. Thermal hysteresis can be seen in the figure. The resistivities of warming curves (symbolized with $\bigcirc$, $\triangle$ and $\square$) are always larger than those of cooling curves (symbolized with $\bullet$, $\blacktriangle$ and $\blacksquare$).
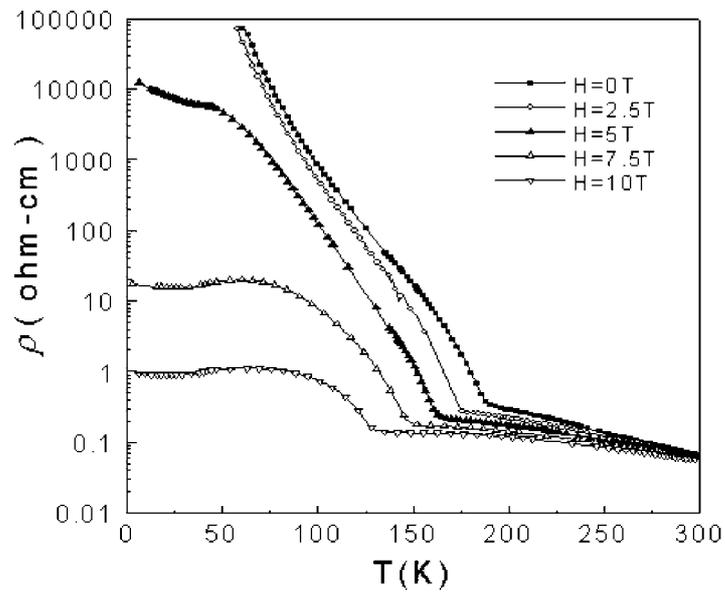
Figure 3. Field dependent resistivity of $Pr_{0.5}Sr_{0.3}Ca_{0.2}MnO_3$. With increasing magnetic field from 0 to 10 T, T_{co} shifts from 190 to 125 K. For $T < T_{co}$, the resistivity decreases with increasing magnetic field.

$Pr_{0.5}Ca_{0.5}MnO_3$, it shows insulator-like behaviour at all temperatures [11]. For $x = 0.1$, 0.2 and 0.3, the TEP shows a slope change at T_c and the absolute value of the TEP decreases with
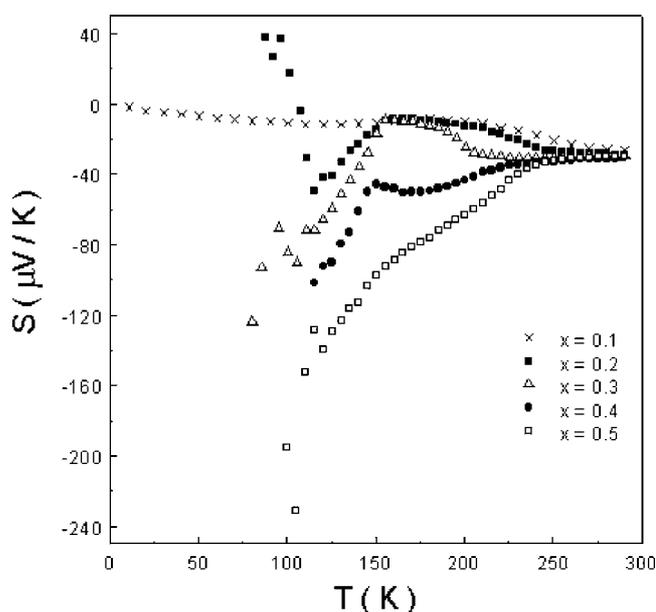
Figure 4. TEP for $Pr_{0.5}Sr_{0.5-x}Ca_xMnO_3$ (cooling only).

decreasing T for $T < T_c$ indicating a metallic behaviour, then it undergoes a metal–insulator transition at T_{co}. Correspondingly, the absolute value of the TEP increases for $T < T_{co}$, displaying an insulator behaviour. But for $x = 0.4$ and 0.5, the change of slope at T_c is not obvious, indicating that the carrier energy does not change significantly. For $T < T_{co}$, the measurement cannot be made because of the high resistance.

In figure 5, the TEP in $Pr_{0.5}Sr_{0.5-x}Ca_xMnO_3$ also shows thermal hysteresis. All the samples show thermal hysteresis between T_c and T_{co}. The TEP for the cooling curves are always larger (less negative) than that of the warming curves. Our measurement is reproducible both for cyclic cooling and warming runs. The fact that the thermal hysteresis still exists even stabilizing for 25 min indicates the unusual robustness of the supercool or superwarm states. It is important to note that the hysteresis loop only exists between T_c and T_{co} in samples of $x = 0.1$ to 0.3. The phenomenon clearly supports our argument that there is a strong competition between the double exchange interaction and the charge ordering. For $x = 0.4$ and 0.5, although the charge order state dominates below 200 K, hysteresis of the TEP still can be observed. This suggests that the competition still occurs in $x = 0.4$ and 0.5. Hence our observation indicates the coexistence of ferromagnetic metallic state and charge ordering state below T_{co} [12].

The first order transition is manifest in the area enclosed by the hysteresis loop of TEP, therefore, the area of hysteresis loop can be taken as a quantitative measure of the robustness of the thermal hysteresis. The thermal hysteresis is strong for $x = 0.3$, and 0.4, but it is small for $x = 0.1$ and $x = 0.5$. For $x = 0.1$ and $x = 0.5$, their low temperature states are dominated by the double exchange and the charge ordering effect, respectively. Correspondingly, their thermal hysteresis is less significant. The contrast between $x = 0.1$, 0.5 and $x = 0.3$, 0.4 suggests that the competition between delocalization and localization effects becomes intense for $x = 0.3$ and 0.4. Although one may be inclined to attribute the thermal hysteresis to the competition of different types of antiferromagnetic state (A type or
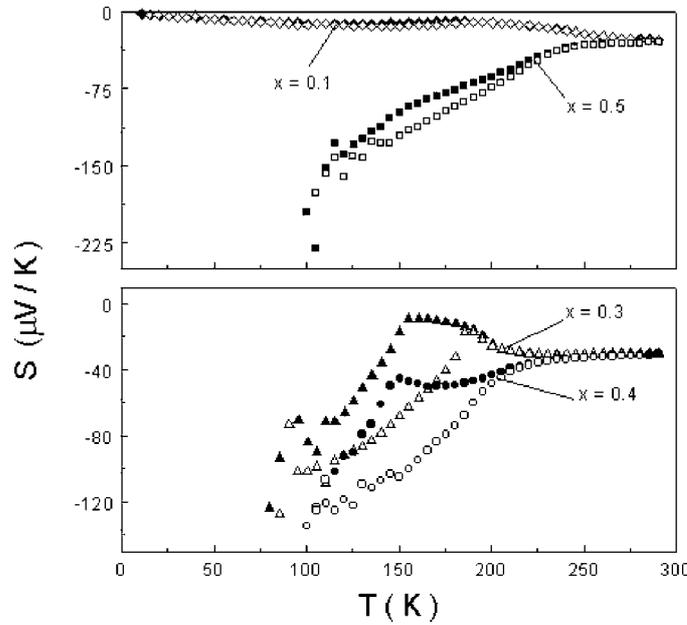
Figure 5. The hysteresis of TEP for $x = 0.1, 0.5$ (upper panel) and for $x = 0.3, 0.4$ (lower panel). The cooling and warming curves are represented as solid and open symbols, respectively. Notice that the areas enclosed by the hysteresis for $x = 0.3$ and 0.4 are relatively larger than those of $x = 0.1$ and 0.5.

CE type), we found the argument not plausible. Since T_N values are always below 180 K for all x irrespective of different types of antiferromagnetic ordering, it is difficult to explain the observed thermal hysteresis in the range of 100–230 K [3]. Moreover, the separation of T_{co} and T_N for $x > 0.3$ indicates that it is the appearance of the charge ordering that freezes the hopping of electrons at a higher temperature and subsequently helps the superexchange antiferromagnetic state to form at a lower temperature. So the antiferromagnetic ordering should be attributed to the formation of the charge ordering state. Finally, the A-type and CE-type antiferromagnetic ordering appears for $x < 0.09$ and $x > 0.09$ [3], which is inconsistent with the maximum thermal hysteresis observed for $x = 0.3$ and 0.4. Therefore, we propose that the thermal hysteresis originates from the competition between delocalization and localization assisted by the double exchange and charge ordering, respectively. Further support comes from the evidence by Hejtmánek *et al* [13], that no strong hysteresis of TEP is observed in Sm$_{0.2}$Ca$_{0.8}$MnO$_3$. Sm$_{0.2}$Ca$_{0.8}$MnO$_3$ is dominated by the charge ordering at temperatures below 150 K and no ferromagnetic state is observed. Thus it is the predominant charge ordering state in Sm$_{0.2}$Ca$_{0.8}$MnO$_3$ that suppresses the thermal hysteresis of the TEP. On the other hand, Tokura *et al* show that the hydrostatic pressure on (Nd$_{0.125}$Sm$_{0.875}$)$_{1/2}$Sr$_{1/2}$MnO$_3$ induces a large shift in $\Delta T_{co} \sim 20$ K [14]. Based on our estimation shown earlier, the pressure effect can only shift $\Delta T_{co} \sim 2$ K if we assume the typical compressibility value $\Delta r/r$ to be <1% [12]. The double exchange interaction must be taken into account to explain the hydrostatic pressure effect on (Nd$_{0.125}$Sm$_{0.875}$)$_{1/2}$Sr$_{1/2}$MnO$_3$. In fact, Kuwahara *et al* [15] has used the words 'charge liquid' for the system with Mn^{3+}/Mn^{4+} = 1. The charge liquid is just a state with the coexistence of the double exchange and the charge ordering interaction.

4. Summary

In summary, $Pr_{0.5}Sr_{0.5-x}Ca_xMnO_3$ shows a ferromagnetic ordering at high temperature and a charge ordering combined with antiferromagnetic ordering at low temperature. By varying the A size, T_{co} can be varied by $\sim$70 K in $Pr_{0.5}Sr_{0.5-x}Ca_xMnO_3$. We have estimated the electrostatic energy variation due to the change of the A size and the lattice contraction. Our results show that the electrostatic energy itself cannot explain the large variation of T_{co}. A strong hysteresis in $Pr_{0.5}Sr_{0.5-x}Ca_xMnO_3$ in the temperature range between T_c and T_{co} has been observed. We regard the distinct thermal hysteresis exhibited in $Pr_{0.5}Sr_{0.5-x}Ca_xMnO_3$ as the manifestation of the competition between the delocalization and localization effect assisted by the double exchange interaction and charge ordering, respectively. This underlying competition results in some observed physical features listed below: (1) the A-size effect can depress the T_{co} by $\sim$70 K for $Pr_{0.5}Sr_{0.5-x}Ca_xMnO_3$; (2) large thermal hysteresis in resistivity and TEP is exhibited in $Pr_{0.5}Sr_{0.5-x}Ca_xMnO_3$; (3) the thermal hysteresis is larger for $x = 0.3$ and 0.4 than that for $x = 0.1$ and 0.5 and (4) magnetic field induces a large shift of T_{co}.

Acknowledgments

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