The reentrant behaviour of spin-glass phase in $(La,Pr)_{0.5}Ca_{0.5}MnO_3$ manganites

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Reentrant spin-glass phase behaviour was reported for $La_{0.5}Ca_{0.5}MnO_3$ and $Pr_{0.5}Ca_{0.5}MnO_3$. ac susceptibility curve for both compounds is very similar and a cusp appears at ~40K after T_C. The $\rho(T)$ measured in a field of 8 T appears M-I transition, but at lower temperature, the resistivity becomes an insulator again. The $M(H)$ gives the presence of FM clusters in the $La_{0.5}Ca_{0.5}MnO_3$. Our data indicate that both $Pr_{0.5}Ca_{0.5}MnO_3$ and $La_{0.5}Ca_{0.5}MnO_3$ compounds have the same ground state, which shows the existence of some FM clusters in the background of remaining region in a spin frozen state

INTRODUCTION

In mixed-valent manganese oxides, the strong correlations among spin, orbital, and lattice degrees of freedom play important roles [1-2]. Especially for the intermediate-hole doped $R_{0.5}Ca_{0.5}MnO_3$ compounds, being close to AFM CE-type charge ordered (CO) phase, is very interesting. Remarkably, CO in the system can be melted by the application of magnetic fields, x-ray, etc [3]. Recent results show that $<r_A>$ can determine the one-electron bandwidth and CO is observed in materials with small $<r_A>$[4]. Both the $La_{0.5}Ca_{0.5}MnO_3$ and $Pr_{0.5}Ca_{0.5}MnO_3$ have small $<r_A>$, and even smaller for $Pr_{0.5}Ca_{0.5}MnO_3$ ($<r_A>\sim1.18Å$). For $Pr_{1-x}Ca_xMnO_3$ system, though the FMM state is never realized in zero magnetic field, the competition between the FMM and charge ordered antiferromagnetic (COAFM) ground state leads to a an increase of FM tendencies as x decreases below 0.5. While for $La_{0.5}Ca_{0.5}MnO_3$ compounds [5], it has been shown that CO occurs not only in AFM regions but can also occur in FM regions (COFM). On the other hand, accumulating theoretical and experimental evidence indicate that the importance of the phase separation (PS), which shows the coexistence of the submicrometer CO and FMM phase [1-2]. The competition between the coexisting phases opens the possibility for the appearance of locally metastable states. Meanwhile, there are some evidence in the literature tends to the framework of the electronic phase separation, such as spin-glass state et al.[6]. Therefore, studying the magnetic state would be very important for determining the physical properties of mangenties. In this paper, we present resistivity, magnetic susceptibility, and magnetization data for $La_{0.5}Ca_{0.5}MnO_3$ and $Pr_{0.5}Ca_{0.5}MnO_3$ compounds. We have observed the reentrant spin-glass-like phase in both compounds and the relevant result indicates that the two compounds have very similar magnetic structure at low temperature.

EXPERIMENTAL DETAILS

Polycrystalline $La_{0.5}Ca_{0.5}MnO_3$ and $Pr_{0.5}Ca_{0.5}MnO_3$ were prepared by conventional solid-state reaction method. Powder XRD measurement revealed that the samples crystallization is good enough, and both samples show good single-phase orthorhombic structure. Magnetic measurements were carried out using physical property measurement system (PPMS) with the precision 20nV for voltage. All the $M(H)$ curves were recorded after the sample were ZFC from room temperature. Transport measurements were carried out using the conventional four-probe technique. The resistivity vs temperature ($\rho(T)$) curves measured under applied DC magnetic fields ranges from 0-8 T were recorded by PPMS in the range of 1.9-300K.

RESULTS AND DISCUSSION

Figure 1 shows the result of ac susceptibility for $La_{0.5}Ca_{0.5}MnO_3$ vs ac field at 2 Oe, 6 Oe, 8 Oe and 10Oe, respectively. For our measurement, the low ac magnetic field is not supposed to affect the magnetic state of the sample. It must be noted that the curves are obtained by the continuous transform measurement between four frequencies (77, 333, 4577 and 1000Hz) and four fields as the temperature change. The transition of T_C is strongly hysteretic which display the first-order-type transition in the system. From the result of the ac magnetic susceptibility as shown in figure 1, we can also observe that the existence of two kinks for the warming curve which is at around 215 and 40 K, respectively. However, for the cooling
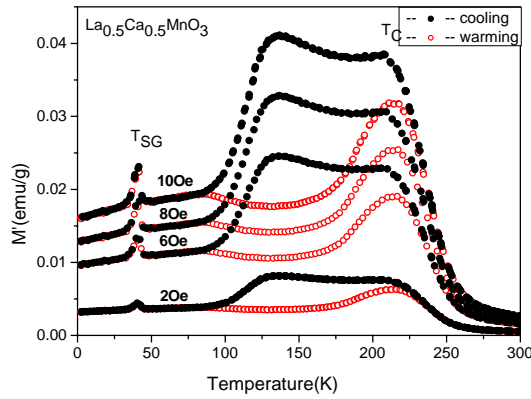

Figure1, Temperature dependence of susceptibility for $La_{0.5}Ca_{0.5}MnO_3$ as a function of ac field at 2 Oe, 6 Oe, 8 Oe and 10 Oe, respectively.
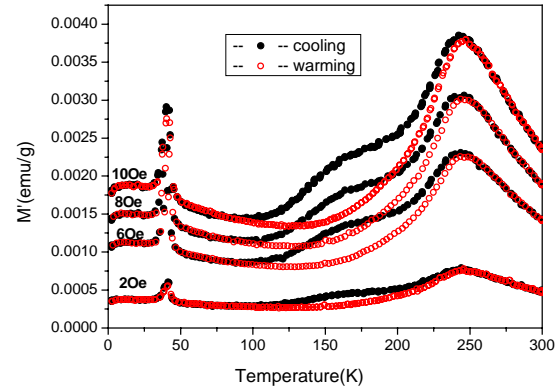

Figure 2, Temperature dependence of susceptibility for $Pr_{0.5}Ca_{0.5}MnO_3$ as a function of ac field at 2 Oe, 6 Oe, 8 Oe and 10 Oe, respectively.

curve, the kink at 215K，which is corresponding to the Curie temperature T_C, becomes more splinted and even appear a plateau between the range of temperature 130~210K. This phenomena may be related to the memory effect which has been detected in bilayer manganite $(La_{1-z}Pr_z)_{1.2}Sr_{1.8}Mn_2O_7$ (z=0.6) single crystal [8] and double layered thin film of LSMO[9]. For the cooling curve, as temperature decreases, the χ_{ac} increases and reaches to its maximum value at around 210K, and then it retain the value until 130K due to the memory effect. While the warming curve retain its AFM state as temperature increases until ~210K. Both behaviors show the FM fraction in the system after the T_C and which is highly temperature sensitive and history-dependent [8]. It should be remarkable that the cusp appeared at ~40K with the temperature decrease as shown in figure 1, it may be related to the low temperature spin-glass behavior which has been reported by De Terai et al [6]. Which presumably is due to the frustration caused by the competition between FM (double exchange) and AFM (super-exchange) interactions. Interestingly, such
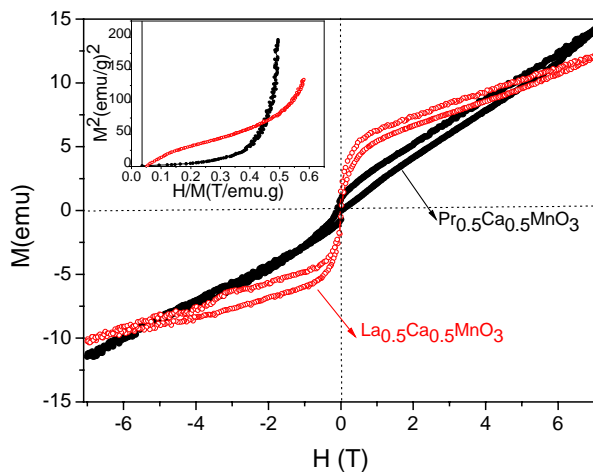

Figure 3, Magnetic field (H) dependence of M for $La_{0.5}Ca_{0.5}MnO_3$ (the red curve) and $Pr_{0.5}Ca_{0.5}MnO_3$ (the blue curve) at 3K, respectively.

behavior occurs after the T_C, so it should belong to reentrant spin-glass behavior. That is to say, the compound undergoes two phases transition as the temperature decreases. The first is from magnetic disordering to long-range magnetic ordering at T_C, and second is from magnetic ordering to spin freezing disordering at the temperature of spin-glass transition (T_{SG}). Which is typically a feature of reentrant spin-glass. At T_{SG}, the Mn ion spin changes from the ferromagnetic long-range magnetic order to the ferromagnetic short-range order of the spin-glass state at enough low temperature. Similar temperature dependences of M/H due to the spin-glass state have been observed also for other compounds [10] and neutron diffraction and ac susceptibility were done to

confirm it. Generally, the T_{SG} is mostly a constant and this is consistent with present property of the cusp at ~40K. Figure 2 shows the ac susceptibility curve for $Pr_{0.5}Ca_{0.5}MnO_3$, which is recorded in the same conditions as that of $La_{0.5}Ca_{0.5}MnO_3$. Interestingly, the behavior of ac susceptibility for $Pr_{0.5}Ca_{0.5}MnO_3$ is very similar to that of $La_{0.5}Ca_{0.5}MnO_3$ as shown in figure 2, except that there didn't appear a plateau between certain ranges of temperature for cooling curve. And the corresponding two kink appear at ~245K and ~40K, respectively. Though the COAFM is the ground state, its small energy difference with the FM state can indicate a tendency towards phase coexistence. This probably can explain the appearance of the cusp at ~40K. There are some trends in the literature pointing to an explanation of the feature in the framework of the electronic phase separation scenario [2], but we suggest it is probably that this electronic phase separation is spin-glass-like state.

In figure 3, the field dependence of magnetization is shown for $La_{0.5}Ca_{0.5}MnO_3$ and $Pr_{0.5}Ca_{0.5}MnO_3$ at 3K, respectively. It can be

Figure 4, The temperature dependence of the resistivity for $La_{0.5}Ca_{0.5}MnO_3$ and $Pr_{0.5}Ca_{0.5}MnO_3$ in the absence of a magnetic field and under magnetic fields of 8 T. The black and red curves stand for cooling and warming process, respectively

seen that the curve slop increases as the magnetic field increases and there shows a noticeable irreversibility for measurement of increasing and decreasing field. However, there is not remanent magnetization when field is zero, which indicates that present irreversibility is due to spin-glass behavior [11]. Both the M vs H curve didn't appear the sign of saturation when the applied magnetic field is 7T. The absence of saturation at 7T correlate well with the high resistivity value as shown in figure 4 which gives the temperature dependence of the resistivity for $La_{0.5}Ca_{0.5}MnO_3$ and $Pr_{0.5}Ca_{0.5}MnO_3$ in the absence of a magnetic field and under magnetic fields of 8 T. The negative value of the magnetization confirms the existence of AFM interaction. Especially for $La_{0.5}Ca_{0.5}MnO_3$, though behaves a noticeable FM behavior at low temperature, the magnetization continuously increase as the magnetic field, which show the presence of some FM clusters in the background of remaining region in a frozen state. The inset of figure 3 gives the Arrott plots obtained from the relative magnetization isotherms at 3K. From which, we can see that there are no sign of spontaneous magnetization and it is not belong to long-range FM ordering state. According to these results, we may also explain the COFM occurred in $La_{0.5}Ca_{0.5}MnO_3$ at 90K. This character of COFM is very difficult to understand according to the conventional models. The tight relationship between COFM and spin-glass phase in the compound may be explained with the temperature decreasing as follows. At high temperature the compound is paramagnetic, and as the temperature is lowered there is a gradual CO which increases the resistivity. If the enough magnetic field is applied, the compound becomes ferromagnetic and a first-order I-M transition takes place at T_C. However, if the applied magnetic field is zero, the sample is composed of an inhomogeneous mixture of ferromagnetic regions and regions with no net magnetization at 90K[5]. On the other hand, at lower temperature, the spin-glass state rather than the ferromagnetic phase sets in which shows the development of competition between the AFM and FM as the temperature decreases. Applying magnetic field in the spin-glass state brings about a reduction in the AFM and the FM clusters appear in the background of remaining region in a frozen state. From figure 4, it can be seen that both the resistivity of $La_{0.5}Ca_{0.5}MnO_3$ and $Pr_{0.5}Ca_{0.5}MnO_3$ under zero-field is insulating. Application of a magnetic field drastically modifies such an insulating state and a M-I transition take places. Meanwhile, the transition becomes strongly hysteretic which display the first-order-type transition in the system. In the inset of figure 4, we give the magnified curves of $\rho(T)$ measured in a field of 8 T. The present transport results indicate that $La_{0.5}Ca_{0.5}MnO_3$ exhibits M-I transition at about 84K (for cooling curve) and the compound shows a metallic behavior in the temperature range of 84~28K. Whereas at lower temperature, $La_{0.5}Ca_{0.5}MnO_3$
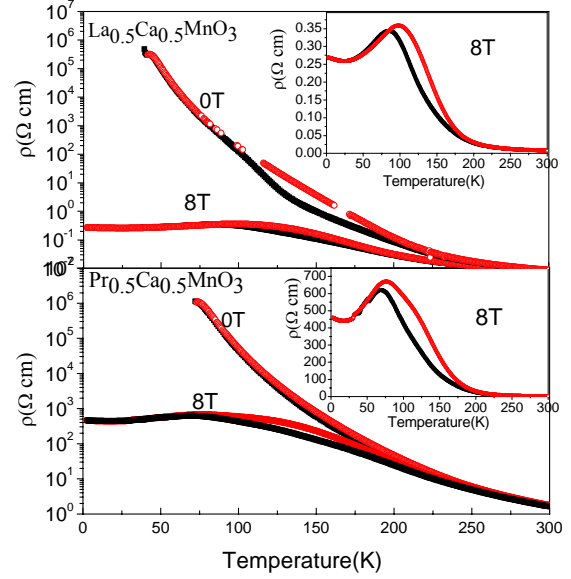
becomes an insulator and show its dramatic increase in resistivity. This may be due to the localization of the charge carriers below temperature of spin-glass transition. We can conjecture a scenario in which localization may occur as follows: According to the DE model, the e_g electron can hop from Mn^{3+} to Mn^{4+} if the two moments are parallel. However, the reentrant spin-glass behavior, as mentioned above, can cause the random freezing of Mn^{3+} and Mn^{4+} moments and thus favors the localization of the e_g electron. In connection with the results of M(H) above, though there are FM cluster formation in the frozen region domain , the system possibly can not find a percolation path through the frozen region and so the resistivity appears second upturn below T_{SG}.

To sum up, using the measurement of resistivity, ac susceptibility and *M(H)*, we have shown that $La_{0.5}Ca_{0.5}MnO_3$ and $Pr_{0.5}Ca_{0.5}MnO_3$ at ~40K, show the existence of reentrant spin-glass behavior. Meanwhile, the result of *M(H)* for $La_{0.5}Ca_{0.5}MnO_3$ at 3K gives the presence of FM clusters. Based on the similar behavior in ac susceptibility, we suggest that there should also exist the competition between AFM and FM in $Pr_{0.5}Ca_{0.5}MnO_3$. All the rich variety of phases can coexist in the manganites is because the bandgap can be locally modified by strain within each grain [12] and other factors. Our results indicate that both compounds have the same ground state which shows the presence of some FM clusters in the background of remaining region in a spin frozen state.

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