Reentrant Spin Glass Behaviour and CE-Type Antiferromagnetic Phase in Half Doping (La,Pr)$_{1/2}$Ca$_{1/2}$ MnO$_3$ Manganites *

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The reentrant spin glass behaviour was observed in half doping (La,Pr)$_{1/2}$Ca$_{1/2}$MnO$_3$ manganites with a CE-type antiferromagnetic structure. It shows sequential multiple magnetic transitions from the paramagnetic to the ferromagnetic, antiferromagnetic, spin glass (SG) transitions, which reflects the complex magnetic interaction in the ground state of manganites. This can be explained by the competition interaction between the ferromagnetic and the CE-type antiferromagnetic matrix, and the disorder due to the tolerance factor t and A-cation size variance σ^2. The results reveals the coexistence of ferromagnetic clusters and SG clusters in the background of the antiferromagnetic matrix in the ground state of half doping (Pr,La)$_{1/2}$Ca$_{1/2}$MnO$_3$ systems.

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The strong correlations between spin, orbital, and lattice degrees of freedom play important roles in mixed-valent manganese oxides.[1,2] The intermediate-hole doped $R_{1/2}Ca_{1/2}MnO_3$ compounds, generally with relatively small $\langle r_A \rangle$ and the CE-type antiferromagnetic structure,[3] are very interesting. Both $La_{1/2}Ca_{1/2}MnO_3$ and $Pr_{1/2}Ca_{1/2}MnO_3$ have small $\langle r_A \rangle$, even smaller for $Pr_{1/2}Ca_{1/2}MnO_3$ ($\langle r_A \rangle \sim 1.18$ Å). For $Pr_{1-x}Ca_xMnO_3$ systems, though the FMM state is never realized in zero magnetic field, the competition between the FMM state and the charge-ordering antiferromagnetic ground state leads to an increase of ferromagnetic tendency as x decreases below 0.5. For $La_{1/2}Ca_{1/2}MnO_3$,[4] it has been proven that charge ordering occurs not only in antiferromagnetic regions but also in ferromagnetic regions. There is some evidence in the literature tending to the framework of the electronic phase separation, such as spin-glass state, etc.[5] In this Letter, we present resistivity, magnetic susceptibility, and magnetization data for the $(La,Pr)_{1/2}Ca_{1/2}MnO_3$ compounds. The results indicate the complex magnetic structure at low temperature due to the competition of the double exchange interaction and the superexchange interaction.

$La_{1/2}Ca_{1/2}MnO_3$ and $Pr_{1/2}Ca_{1/2}MnO_3$ samples were prepared by the solid-state reaction method. Magnetic measurements were carried out using physical property measurement system. The resistivity versus temperature was measured in the presence of applied dc fields from 0–8 T and in the temperature range 1.9–300 K.

Figure 1 shows the result of ac susceptibility versus ac field at 2, 6, 8 and 10 Oe, respectively, for $La_{1/2}Ca_{1/2}MnO_3$. The curves appear strongly hysteretic near T_C, which displays the first-order-type transition and, for the warming curve, there are two kinks around 215 and 41 K. However, for the cooling curves, the kink at 215 K, i.e. Curie temperature T_C, becomes more gentle and then a plateau appears in the range 130–210 K. With decreasing temperature, the magnetic susceptibility χ_{ac} increases to a maximum value around 210 K and then remains unchanged until 130 K, while for the warming curve, it retains antiferromagnetic behaviour until $\sim$ 210 K. It is obvious that the magnetic properties for warming and cooling processes are highly temperature-sensitive and history-dependent.[6] For the kink at $\sim$ 41 K, this may be related to the spin-glass behaviour at low temperature, which was thought to be due to the frustration caused by the competition between the ferromagnetic (double exchange) and antiferromagnetic (super-exchange) interactions as reported by de Terai *et al.*[7] Interestingly, such behaviour occurs below T_C and shows the reentrant characteristic of the spin-glass behaviour. That is to say, this compound undergoes two phase transitions as the temperature decreases. The first is from magnetic disordering to long-range ordering at T_C, and the second is from magnetic ordering to spin frozen disordering at the SG transition temperature (T_{SG}). This is a typical characteristic of reentrant SG. Figure 2 shows the ac susceptibility curve for $Pr_{1/2}Ca_{1/2}MnO_3$, which is recorded under the same conditions as $La_{1/2}Ca_{1/2}MnO_3$. It can be seen that, except for a wide ferromagnetic plateau in $La_{1/2}Ca_{1/2}MnO_3$ at cooling curve, both the curves are very similar. This also indicates successive paramagnetic–ferromagnetic–antiferromagnetic–reentrant SG transitions, and the corresponding two

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kinks appear at $\sim$ 245 K and $\sim$ 40 K, respectively. For the ground state of the half-doping system, in spite of the charge ordering-antiferromagnetic state domains,[8] the small energy difference from the ferromagnetic state can indicate a tendency towards phase coexistence. This will probably explain the appearance of the cusp at $\sim$ 40 K in the framework of the electronic phase separation with the SG-like state.

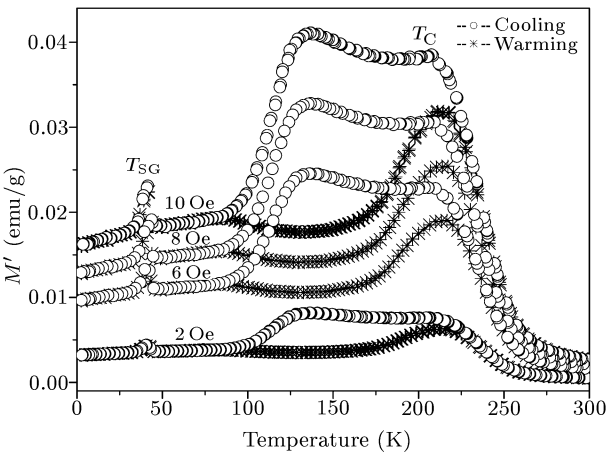


Fig. 1. Temperature dependence of ac susceptibility for $La_{1/2}Ca_{1/2}MnO_3$ at ac field of 2, 6, 8 and 10 Oe, respectively.

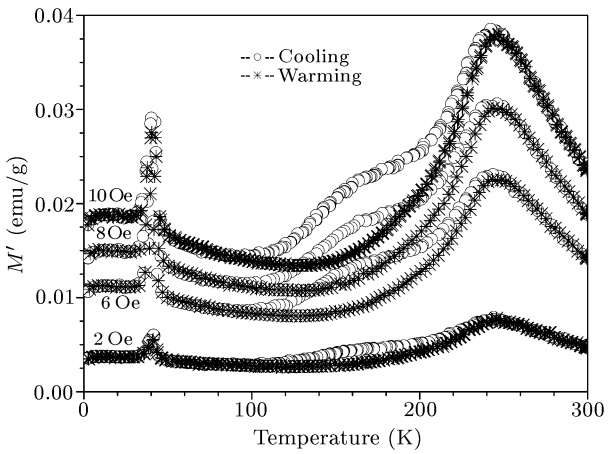


Fig. 2. Temperature dependence of ac susceptibility for $Pr_{1/2}Ca_{1/2}MnO_3$ at ac field of 2, 6, 8 and 10 Oe, respectively.

From the results of XRD, the calculated lattice parameters and other details are listed in Table 1. It has shown that the properties of manganites strongly depend on a geometrical quantity called the tolerance factor t and the A-cation size variance σ^2 (corresponding to a random distribution of Mn–O–Mn bond angles),[9] which are defined as $t = \dfrac{\langle r_A\rangle + r_O}{\sqrt{2}(r_{\rm Mn} + r_{\rm O})}$ and $\sigma^2 = \langle r_A^2\rangle - \langle r_A\rangle^2$, respectively. Here $\langle r_A\rangle$ is the average A-cation radius, and $r_{\rm Mn}$ and r_O are the radii of the manganese and oxygen ions, respectively. The values of t and σ^2 for $La_{1/2}Ca_{1/2}MnO_3$ and $Pr_{1/2}Ca_{1/2}MnO_3$ are also listed in Table 1. In the present experiment, the observed SG state is not a typical SG phase appeared in a variety of disordered magnetic systems but a reentrant SG characteristic.[10] For a typical SG system, t and σ^2 will play important roles for this electron inhomogeneous SG phase. The tolerance factor $t \leq 0.906$ will prevent the occurrence of long-range magnetic ordering due to the competition between the ferromagnetic double-exchange (DE) and the antiferromagnetic superexchange interaction, and then the SG state sets in.[10] This is a typically uniform electronic phase separation for conventional SG systems. The present reentrant SG behaviour in $(La,Pr)_{1/2}Ca_{1/2}MnO_3$ systems is very peculiar due to its small variance of ionic sizes in A sites. Here the values of t and σ^2 are 0.924 and 3.05×10^{-4} Å^2 for $La_{1/2}Ca_{1/2}MnO_3$, and 0.917 and 1.22×10^{-5} Å^2 for $Pr_{1/2}Ca_{1/2}MnO_3$, respectively. For the present $(La,Pr)_{1/2}Ca_{1/2}MnO_3$, $t \geq 0.918$, which is larger than 0.906. Combined with the cusp-like anomaly found in χ_{ac} at $T_f \approx 41$ K, it should show the existence of a disordered cluster-glass state. This behaviour can also be explained by taking σ^2 in consideration because the smaller the t value is, the higher the value of σ^2 is, and this will cause an increase of inhomogenieity in the sample due to the mismatch of the sizes of the A sites cations doped in the mother manganites $CaMnO_3$. For the present compounds, although the variance of mismatch is smaller than other manganites such as $R_{1/2}A_{1/2}MnO_3$ (R=Gd, Dy, Ho, Er; A=Sr, Ca), it induces the appearance of disorder in some regions at low temperature and then causes a reentrant SG change. Recently, a scenario of the electronic phase separation has been raised as a general feature in the manganites and cuprates systems.[11] It is shown that a quenched disorder induced by the random ion replacement in A sites plays an important role in determining the size of coexisting clusters in the inhomogeneous systems. On this aspect, Levy *et al.*[11] found that the fraction of the ferromagnetic phase gradually decreases as the grain size increases and suggests that the grain boundaries play a distinctive role for the spatial distribution of coexisting phases. Other experimental data reported on the polycrystalline sample show that the clusters in the phase-separated systems are affected more seriously by the grain boundaries than by the random potential due to the ions substitution alone. This viewpoint is also borne out by the fact that the SG behaviour was not found in prevenient works,[12] which is possibly related to the grain boundaries and should be sensitive to different thermal processes. Nevertheless, for $Pr_{1/2}Ca_{1/2}MnO_3$, the two cations sharing the A site in the structure have very similar ionic sizes (1.126 Å for [Pr^{3+}] and 1.12 Å for [Ca^{2+}]). This represents a

very important feature that the local strain effect originated from the size distribution of the A-site cations is completely minimized in $Pr_{1/2}Ca_{1/2}MnO_3$. However, the reentrant SG was indeed found in the present experiments, so we can suppose that the magnetic behaviour is very sensitive to a small disorder at low temperature and the cluster reentrant SG should be a universal phenomenon for the ground state of the manganites due to the spin freezing by subtle disorder. The SG cluster may present the coexistence of SG and some kinds of magnetic ordered states. From the above results we can conclude that the CE-type antiferromagnetic manganites display the coexistence of ferromagnetic clusters and antiferromagnetic matrix at low temperature. And below the temperature of T_{SG}, some spin will be frozen due to the lattice distortion and forms some SG cluster, which displays the antiferromagnetic-cluster nature of SG.

Table 1. Experimental and calculated lattice constants $\langle r_A \rangle t$ and σ^2 for $(La,Pr)_{1/2}Ca_{1/2}MnO_3$.

Sample	Lattice constants (Å)			$\langle r_A \rangle$ (Å)	Tolerance factor (t)	σ^2 (Å^2)
	a	b	c			
$La_{1/2}Ca_{1/2}MnO_3$	5.4173	7.6400	5.4289	1.19	0.924	3.049×10^{-4}
$Pr_{1/2}Ca_{1/2}MnO_3$	5.4086	7.6082	5.4209	1.18	0.918	1.22×10^{-5}

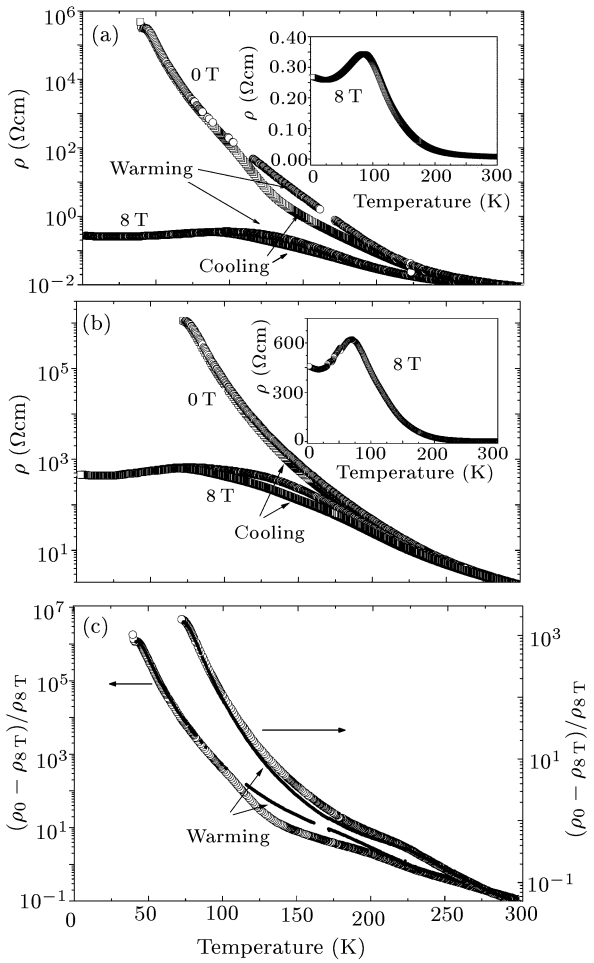


Fig. 3. Temperature dependence of the resistivity in the absence of a magnetic field and under magnetic fields of 8 T for (a) $La_{1/2}Ca_{1/2}MnO_3$ and (b) $Pr_{1/2}Ca_{1/2}MnO_3$ (c) Magnetoresistance as a function of temperature at 8 T. The insets give the enlarged $\rho(T)$ curves at a field of 8.0 T.

The temperature dependence of the resistivity for $La_{1/2}Ca_{1/2}MnO_3$ and $Pr_{1/2}Ca_{1/2}MnO_3$ are given under a magnetic field of zero and 8 T in Fig. 3. It can be seen that, under zero-field, both are all insulating. The applied field of 8 T drastically modifies such an insulating state and a metal–insulating transition appears. Meanwhile, the metal–insulating transition becomes strongly hysteretic with a typical characteristic of first-order phase transition. The insets give the magnified $\rho(T)$ curves at a field of 8 T in Fig. 3(a) and 3(b), respectively. It can be seen that the transport behaviour for $La_{1/2}Ca_{1/2}MnO_3$ and $Pr_{1/2}Ca_{1/2}MnO_3$ are very similar except the value of the residual resistivity, which the former is smaller than the later. The present results indicate that $La_{1/2}Ca_{1/2}MnO_3$ exhibits a metal–insulating transition at about 84 K (for cooling curve) and a metallic behaviour in a temperature range of 84–28 K. Whereas at lower temperature, $T > 22$ K, it becomes an insulator by a dramatic increase in resistivity. This may be due to the localization of the charge carriers below reentrant SG transition temperature. According to Sheng *et al.* argument,[13] the presence of a certain nonmagnetic randomness and the effective DE hopping disorder could induce an Anderson metal–insulating transition. For present manganites, three features would affect the electronic localization: (i) magnetic disorder; (ii) a local potential fluctuation leaded by La^{3+}/Pr^{3+} substitution with Ca^{2+}, which is comparable with the e_g band width; (iii) the lattice distortion due to different ionic sizes in A sites. The last both can give rise to a rather strong nonmagnetic electron-impurity scattering potential for general Mn oxides. La ion is nonmagnetic ions and its substitution into A sites for Ca will not introduce any magnetic disorder. According to the similarity of the behaviour of reentrant SG appeared in $Pr_{1/2}Ca_{1/2}MnO_3$ to that in $La_{1/2}Ca_{1/2}MnO_3$, the origination of the reentrant SG should be the same as each other in spite of the magnetic moment of Pr ions. Actually, Pr ion has no net moment in the antiferromagnetic matrix at zero field,[14] so the possible magnetic disorder is negligible due to the exchange coupling between Pr $4f$ and Mn $3d$ spins. Consequently, the disorder appeared probably in both the present compounds should mainly be originated from the nonmagnetic disorder and is not related to the magnetic disorder because the present reentrant SG

exits in the background of antiferromagnetic matrix. However, according to the values of t and σ^2 listed in Table 1, we can conclude that the nonmagnetic disorder in both the compounds should be very smaller than other manganites. This may be the origination of coexistence of cluster SG phase and ferromagnetic cluster. This disorder leads to a localization of e_g electrons, which is similar to that pointed out in Anderson localization.[15] From these, we can conjecture that the electronic 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, due to variance of lattice ion or effect of the grain boundary, as mentioned above, the reentrant SG behaviour can cause the random freezing of Mn^{3+} and Mn^{4+} moments and thus favours the localization of the e_g electron. In connection with the results of $M'(T)$ above, though there are ferromagnetic cluster formation in the frozen domain, there is not a percolation possible path through the frozen region in the system and so the resistivity appears a second upturn below T_{SG}.

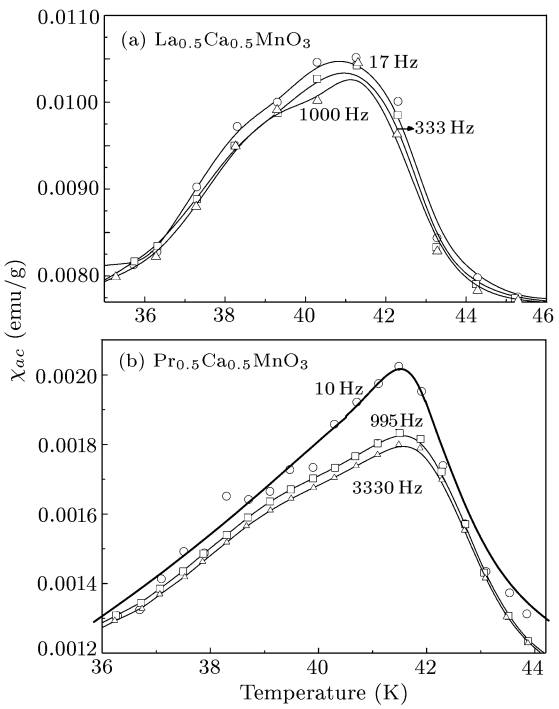


Fig. 4. Susceptibility χ_{ac} at the ac field is 6 Oe and different frequencies, 10, 995 and 3330 Hz, respectively, for the $La_{1/2}Ca_{1/2}MnO_3$ and $Pr_{1/2}Ca_{1/2}MnO_3$ samples.

Figure 4 shows the susceptibility results as a function of temperature at different frequencies for $La_{1/2}Ca_{1/2}MnO_3$ and $Pr_{1/2}Ca_{1/2}MnO_3$, respectively. The curves display a maximum value at a certain temperature and shift upwards the region of high temperature with increasing frequency, which is a distinct feature of as SG state[16] and is consistent with the reentrant SG phase appeared at low temperature for $(La,Pr)_{1/2}Ca_{1/2}MnO_3$. According to conventional critical slowing down model,[17] the present frequency-dependent reentrant SG results can be well described by

$$\frac{\tau}{\tau_0} = \left(\frac{T_f - T_{SG}}{T_{SG}}\right)^{-z\nu}. \qquad (1)$$

Here T_{SG} is the SG transition temperature and T_f is the frequency dependent freezing temperature at which the maximum relaxation time τ corresponds to the measured frequency in terms of $\tau_{\max} = 1/\omega$. Here τ_0 is the characteristic time constant of the spin glass and $z\nu$ is a critical component. Generally, in the case of a conventional spin glass one observed $\tau_0 = 10^{-13}$ s. In the present case for $La_{1/2}Ca_{1/2}MnO_3$ and $Pr_{1/2}Ca_{1/2}MnO_3$, we can calculate the parameters τ_0 and $z\nu$ according to Eq. (1). Here the freezing temperature T_{SG} is determined by extrapolating $T_f - - f$ curve to zero frequency in which the T_f data are obtained from Fig. 4. From this relation, we can obtain $\tau_0 = 4.63 \times 10^{-7}$ s for $La_{1/2}Ca_{1/2}MnO_3$ and $\tau_0 = 2.96 \times 10^{-7}$ for $Pr_{1/2}Ca_{1/2}MnO_3$, respectively. Their corresponding $z\nu$ values are 1.14 and 0.95, respectively. The value obtained here is slightly larger than the rest. The larger τ_0 shows that the systems should be in a more ordering state. Such a difference between the magnitudes of 10^{-7} and 10^{-3} may be attributed to the presence of ferromagnetic clusters of Cr-doped $La_{0.86}Ca_{0.14}Mn_{1-y}Cr_yO_3$ for $y = 0.1$ and 0.2.[18]

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