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Origin of glassy magnetic behaviour in the bilayered manganite $(La_{0.5}Nd_{0.5})_{1.2}Sr_{1.8}Mn_2O_7$

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Abstract

We report a detailed study of the glassy magnetic behaviour in a phase-separated $(La_{0.5}Nd_{0.5})_{1.2}Sr_{1.8}Mn_2O_7$ single crystal. The frequency dependence of the ac susceptibility, as well as ageing and memory effects observed in the sample, are similar to the glassy behaviour in spin glasses. However, the evolution of ac susceptibility with superposed dc fields is contrary to what is expected for a classical spin-glass phase. Instead, it can be well understood in terms of the coexistence of a spin-glass-like phase and an assembly of magnetic clusters in a phase-separated state. Therefore, our study clarifies the origin of glassy behaviour in the bilayered manganite $(La_{0.5}Nd_{0.5})_{1.2}Sr_{1.8}Mn_2O_7$.

(Some figures in this article are in colour only in the electronic version)

1. Introduction

Perovskite manganites have attracted a lot of research interests due to their peculiar physical properties [1, 2]. Depending on the composition and hole-doping level, many manganites exhibit unusual nonequilibrium dynamics and time-dependent phenomena such as ageing, rejuvenation, and memory, etc [3–6]. These phenomena are quite similar in appearance to those observed in classical spin-glasses. Therefore, there is a controversy over the question whether the 'glassy state' in manganites constitutes a classical spin-glass phase or not. Recently, this question has been clarified for several systems of perovskite oxides. Rivadulla *et al* [7] have studied the manganite $(La_{0.25}Nd_{0.75})_{0.7}Ca_{0.3}MnO_3$ and concluded that the glassy behaviour can be understood by taking into account only the intercluster interactions in the phase-separated state. Meanwhile, Tang *et al* [8] have performed a detailed analysis on the magnetic relaxation in $La_{0.82}Sr_{0.18}CoO_3$ and concluded that both the intercluster interactions and a spin-glass-like phase contribute to the glassy behaviour.

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Apart from the $R_{1-x}A_xMnO_3$ manganites, glassy behaviour has also been observed in certain bilayered manganites such as $(La_{0.4}Pr_{0.6})_{1.2}Sr_{1.8}Mn_2O_7$ [9]. However, compared with the $R_{1-x}A_xMnO_3$ manganites, the glassy magnetic behaviour in bilayered manganites with the formula $La_{2-2x}Sr_{1+2x}Mn_2O_7$ has not been studied in detail and the origin of the glassy dynamics still remains an open question. In this paper, we present a detailed study of the glassy behaviour at low temperature in a bilayered manganite $(La_{0.5}Nd_{0.5})_{1.2}Sr_{1.8}Mn_2O_7$. This sample is selected because of its critical composition. Previous studies in $(La_{1-x}Nd_x)_{1.2}Sr_{1.8}Mn_2O_7$ have demonstrated that a ferromagnetic metallic ground state dominates for $x < 0.4$ but an insulating state holds for $x \geqslant 0.6$ [10]. Therefore, $x = 0.5$ is at the boundary between the insulating and metallic states, where a phase-separated state and glassy behaviour are most favoured. By a careful analysis of the ac susceptibility and dc magnetic relaxation in a $(La_{0.5}Nd_{0.5})_{1.2}Sr_{1.8}Mn_2O_7$ single crystal, we clarify that the glassy dynamics is due to the both the intercluster interactions and a spin-glass-like phase in a phase-separated state.

2. Experiments

Single crystals of $(La_{0.5}Nd_{0.5})_{1.2}Sr_{1.8}Mn_2O_7$ were grown in flowing air using a floating-zone optical image four-mirror furnace. A thin platelet-shaped sample with shiny surfaces was cleaved from the crystals. X-ray diffraction (XRD) and back-reflection Laue XRD experiments were taken to check the single crystallinity and determine the crystallographic direction. The flat side of the platelet corresponds to the *ab* plane and accordingly the *c* axis is perpendicular to its surface. Powder x-ray diffraction measurements at room temperature and Rietveld analysis [11] indicate that the crystals were single phase and that the crystal symmetry is tetragonal ($I4/mmm$; $Z = 2$). A piece of $(La_{0.5}Nd_{0.5})_{1.2}Sr_{1.8}Mn_2O_7$ single crystal was cut and chosen to take the measurements. The dc magnetization measurements were performed by using a superconducting quantum interference device magnetometer (Quantum Design MPMS-7). The ac susceptibilities and resistivity were measured by using a commercial physical properties measurement system (Quantum Design PPMS-14T). The dc and ac magnetic field were both applied along the *c* axis of the crystal, which is the easy magnetization direction [12]. In order to obtain a reliable low field, the superconducting magnet was demagnetized before measurements.

3. Results and discussion

We first checked the dc magnetization and resistivity of the $(La_{0.5}Nd_{0.5})_{1.2}Sr_{1.8}Mn_2O_7$ single crystal. Figure 1 shows the zero-field-cooled (ZFC) and field-cooled (FC) magnetization in a 100 Oe magnetic field ($H \parallel c$ axis) as a function of temperature. There is a large divergence between ZFC and FC magnetization below a freezing temperature T_f (~25 K), which suggests that there is no long-range magnetic ordering at low temperature. Figure 2 shows the resistivity of the $(La_{0.5}Nd_{0.5})_{1.2}Sr_{1.8}Mn_2O_7$ single crystal as a function of temperature in different external magnetic fields. Both the current and the field are applied along the *c* axis of the crystal. In zero magnetic field, the sample is insulating down to 32 K (the resistivity along the *c* axis is too large to be measured below 32 K). This is in strong contrast to the metallic behaviour of the parent compound $La_{1.2}Sr_{1.8}Mn_2O_7$ which has a metal–insulator transition at 125 K [13]. In a magnetic field of 5 and 13 T, the resistivity decreases very quickly at low temperature, and a metal–insulator transition is induced. The transition shifts to higher temperature with increasing magnetic field, from 48 K in $H = 5$ T to 130 K in $H = 10$ T. Moritomo *et al* [10] proposed that the field-induced metal–insulator transition is due to a field-induced change in orbital occupancy of the e_g electrons of Mn^{3+}, which favours the $d_{x^2-y^2}$ states with respect to

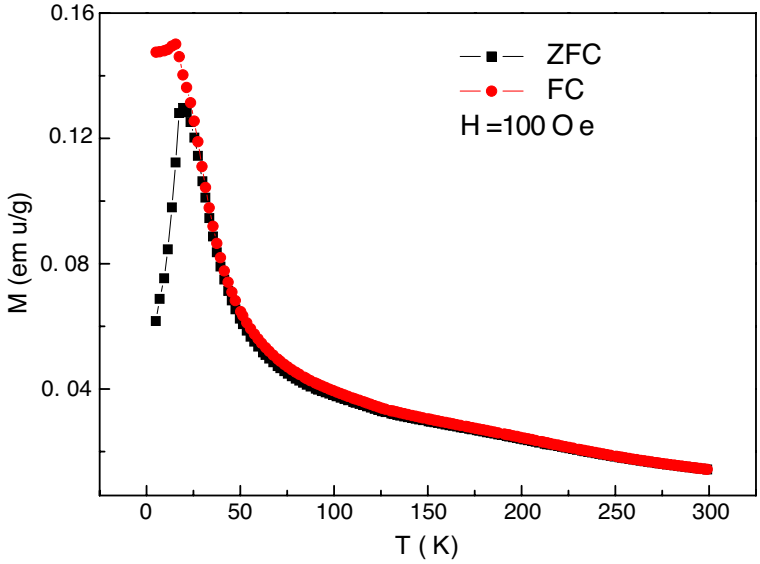

Figure 1. ZFC and FC magnetization of $(La_{0.5}Nd_{0.5})_{1.2}Sr_{1.8}Mn_2O_7$ as a function of temperature in a field of 100 Oe with $H \parallel c$ axis.

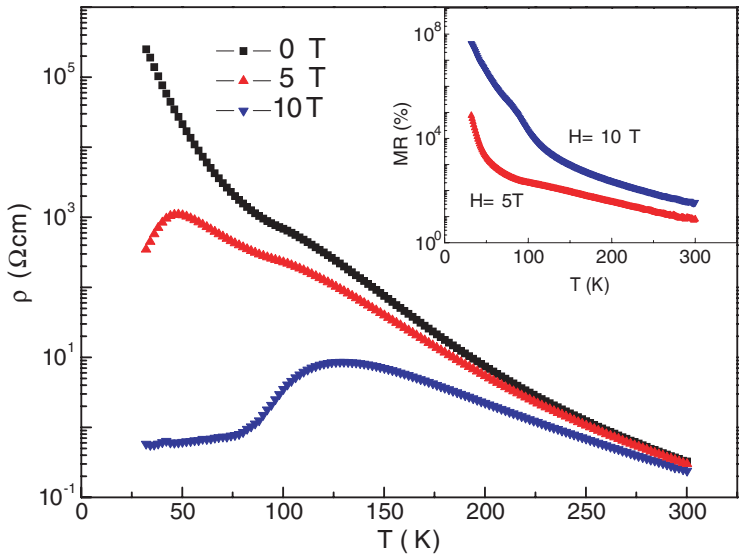

Figure 2. Temperature dependence of c-axis resistivity of $(La_{0.5}Nd_{0.5})_{1.2}Sr_{1.8}Mn_2O_7$ in different magnetic fields. The inset shows the magnetoresistance as a function of temperature.

the $d_{3z^2-r^2}$ states, leading to a long-range ferromagnetic metallic state. The magnetoresistance (MR) is plotted in the inset of figure 2, where MR is defined as $MR = [\rho(0) - \rho(H)]/\rho(H)$. Due to the field-induced insulator–metal transition, a colossal magnetoresistance with an amplitude of eight orders is observed at low temperature.

Then we focus on the low-temperature phase of the crystal. Figure 3 displays the in-phase component of the ac susceptibility, χ', versus temperature for the $(La_{0.5}Nd_{0.5})_{1.2}Sr_{1.8}Mn_2O_7$

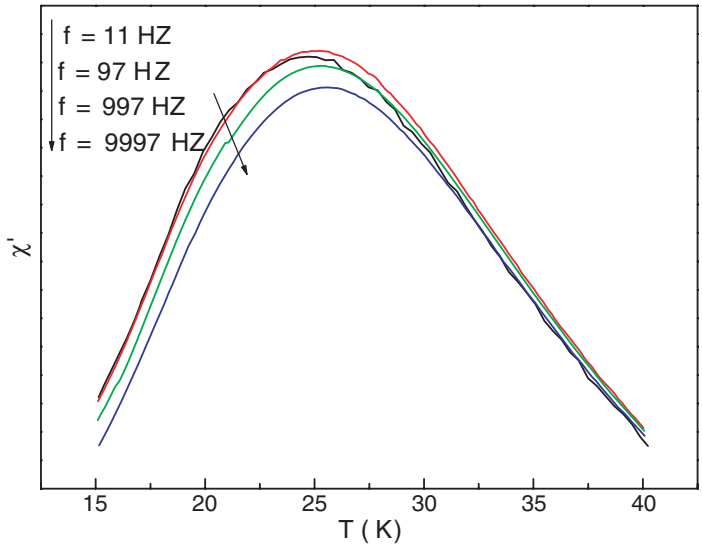

Figure 3. Frequency dependence of the real component (χ') of the ac susceptibility for $(La_{0.5}Nd_{0.5})_{1.2}Sr_{1.8}Mn_2O_7$.

single crystal between 15 and 40 K in a driving field $H_{ac} = 10$ Oe and the frequency range $11 \leqslant f \leqslant 9997$ Hz. χ' shows a maximum at a freezing temperature (T_f) around 25 K, consistent with the dc magnetization. As the frequency increases, the peak temperature increases and the magnitude of the peak decreases, which is similar to the well-known spin-glass behaviour.

In order to further study the glassy behaviour of the sample, we measured the ageing effect which is well-known in spin-glasses and many other random magnetic systems. The sample was cooled in zero field from 300 K to a measuring temperature 15 K, and kept there for a waiting time t_w. After the waiting time, a small probing field of 50 Oe was applied and the magnetization was recorded as a function of time. The magnetic relaxation curves are shown in figure 4. The relaxation can be fitted by a stretched exponential function $M(t) = M_0 + (M_\infty - M_0)[1 - \exp(-(\frac{t}{\tau})^\beta)]$, where M_0 is the initial magnetization at $t = 0$, M_∞ is the magnetization at $t = \infty$, τ is the relaxation time which is related to the magnitude of the energy barrier between two metastable states [14], and β is a dispersion parameter between 0 and 1 associated with the strength of interactions [7]. This function is very similar to the Kohlrausch form [15], which is often used to describe the relaxation in strongly interacting materials. The fitting curves are presented as red solid lines in figure 4. The fitting parameters obtained are summarized in the following. When $t_w = 100$ s, $M_0 = 0.0501$ emu g^{-1}; $M_\infty = 0.0614$ emu g^{-1}; $\tau = 1367.4$ s; $\beta = 0.4418$. As for $t_w = 1000$ s, $M_0 = 0.0497$ emu g^{-1}; $M_\infty = 0.0615$ emu g^{-1}; $\tau = 2627.8$ s; $\beta = 0.4632$. These fitting parameters of τ and β have the same orders of magnitude as those in [12, 16]. The value of τ increases with increasing t_w, which indicates a stiffening of the spin relaxation. To illustrate a waiting time dependence of the magnetic relaxation, it is convenient to use the relaxation rate $S(t)$ defined as $S(t) = (1/H)(\partial M/\partial \ln t)$. The $S(t)$ versus $\log_{10}(t)$ plot is presented in figure 5 for different waiting times. Apparently, the magnetic relaxation depends on the waiting time and a maximum in $S(t)$ is observed at an observation time close to the waiting time (t_w), implying an ageing effect. The ageing effect has usually been interpreted by the droplet

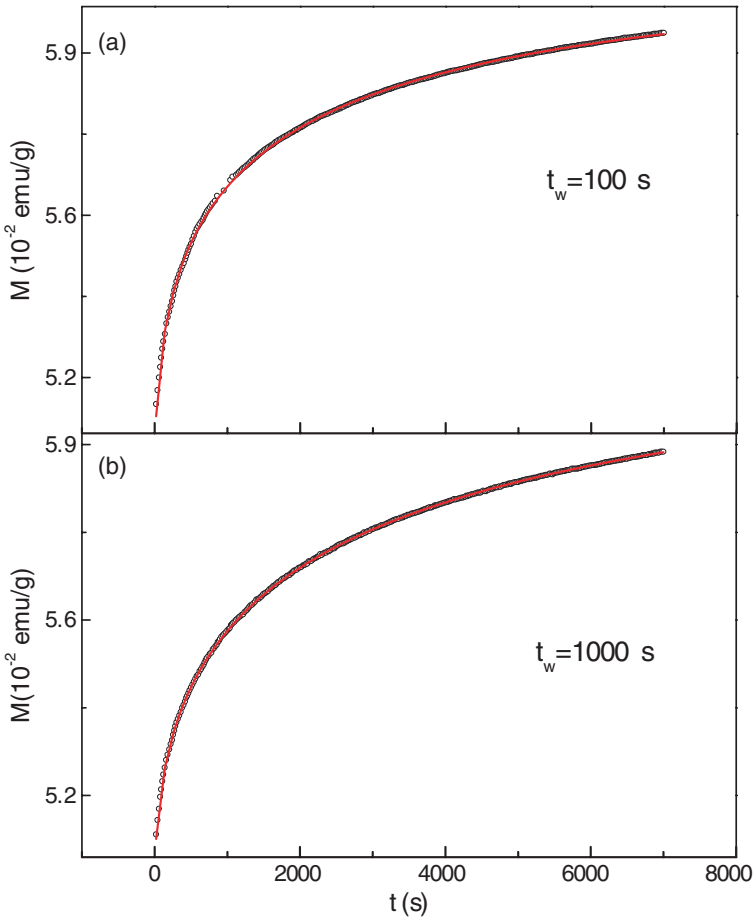

Figure 4. Magnetization as a function of time at $T = 15$ K for different waiting times. The red solid lines are fitting curves (see text).

model [17], in which the maximum of the relaxation rate is associated with a crossover from quasiequilibrium dynamics at short observation times ($t < t_w$) to nonequilibrium dynamics at long observation times ($t > t_w$).

We then demonstrated the memory effect in the crystal. First, the sample of $(La_{0.5}Nd_{0.5})_{1.2}Sr_{1.8}Mn_2O_7$ was zero-field-cooled from 300 to 5 K continuously at a constant cooling rate of 2 K min^{-1}. After the temperature became stable, a 50 Oe field was applied and the magnetization was measured on heating at the same rate up to 50 K. This M–T curve is plotted as the reference curve in figure 6. Then, the sample was cooled again from 300 to 5 K at the same rate in zero field but with a temporary stop at 15 K for 3 h. Finally, the sample temperature was raised continuously at a 2 K min^{-1} rate in a constant 50 Oe field and the magnetization was measured again. This process was repeated with a temporary stop for 3 h at 10 K. These M–T curves were referred as the memory curves, as shown in figure 6. To clearly illustrate the memory effect, it is necessary to compare the differences between the reference and the memory curves, which are also present in figure 6. Clear memory dips are observed at both 15 and 10 K, indicating that the system presents obvious memory behaviour.

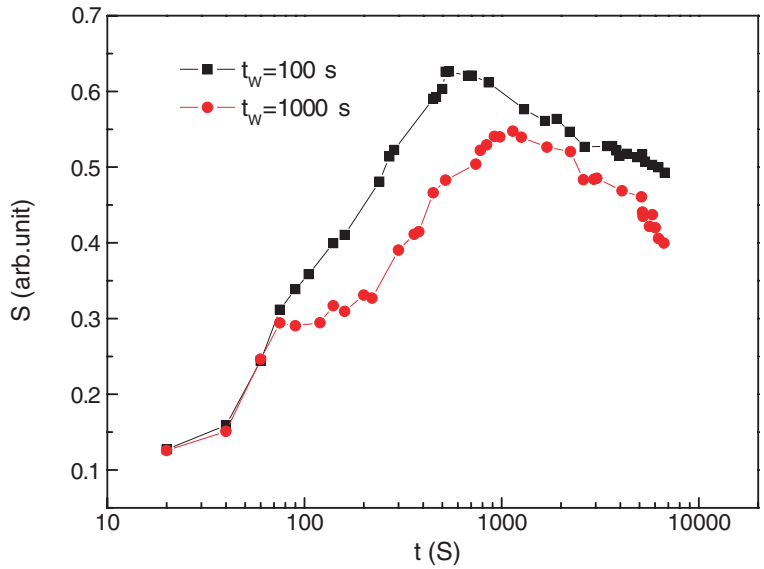

Figure 5. Relaxation function $S(t) = (1/H)(\partial M/\partial \ln t)$ versus $\log_{10} t$ at $T = 15$ K for different waiting times.

The above results clearly demonstrate typical glassy behaviour in $(La_{0.5}Nd_{0.5})_{1.2}Sr_{1.8}Mn_2O_7$. However, the origin of this glassy magnetic behaviour remains unclear because both classical spin-glasses and interacting magnetic clusters could cause such behaviour. The field dependence of ac susceptibility is a good approach to clarify this question. In classical spin-glasses, the peak in ac susceptibility value usually shifts to lower temperature with increasing applied dc field. In contrast, the peak in the ac susceptibility shifts to higher temperatures with increasing dc field in a system of interacting magnetic clusters [7].

The temperature dependence of ZFC ac susceptibility in an ac field of 10 Oe and at a frequency of 11 Hz with different superposed dc fields in $(La_{0.5}Nd_{0.5})_{1.2}Sr_{1.8}Mn_2O_7$ is presented in figure 7. For clarity, the value of χ' in high dc fields has been multiplied by a factor. Interestingly, the peak in ac susceptibility shows a very peculiar dependence on the applied dc field. In zero dc field the ac susceptibility exhibits a pronounced peak at 24.4 K, defined as T_{f1}. With increase of the dc field, the peak broadens and shifts to lower temperature. When the dc field reaches 1 T, another peak at high temperature, defined as T_{f2}, becomes clear, which leads to the coexistence of two peaks in the ac susceptibility. With further increase of dc field up to 9 T, the peak at high temperature becomes more pronounced and shifts to higher temperature while the peak at low temperature becomes invisible.

T_{f1} is shown as a function of dc field in the upper inset of figure 7. It is well known that T_f shifts to lower temperature at higher field in many classical spin-glasses, which can be described by the Almeida–Thouless line $H = H_0[1 - T_f(H)/T_0]^{3/2}$ [18]. In $(La_{0.5}Nd_{0.5})_{1.2}Sr_{1.8}Mn_2O_7$, we found that the data of T_{f1} versus dc field can be fitted nicely using an Almeida–Thouless line, and the solid line is the fitting result. The fitting parameters obtained are as follows: $H_0 = 3.44$ T, $T_0 = 24.68$ K. Such a shift of T_{f1} versus dc field was also observed in $La_{0.82}Sr_{0.18}CoO_3$ [8]. It indicates that there may exist a spin-glass-like phase in the single crystal of $(La_{0.5}Nd_{0.5})_{1.2}Sr_{1.8}Mn_2O_7$. The dc field dependence of T_{f2} is displayed in the lower inset of figure 7. With increase of the dc field, it is obvious that T_{f2} shifts to higher

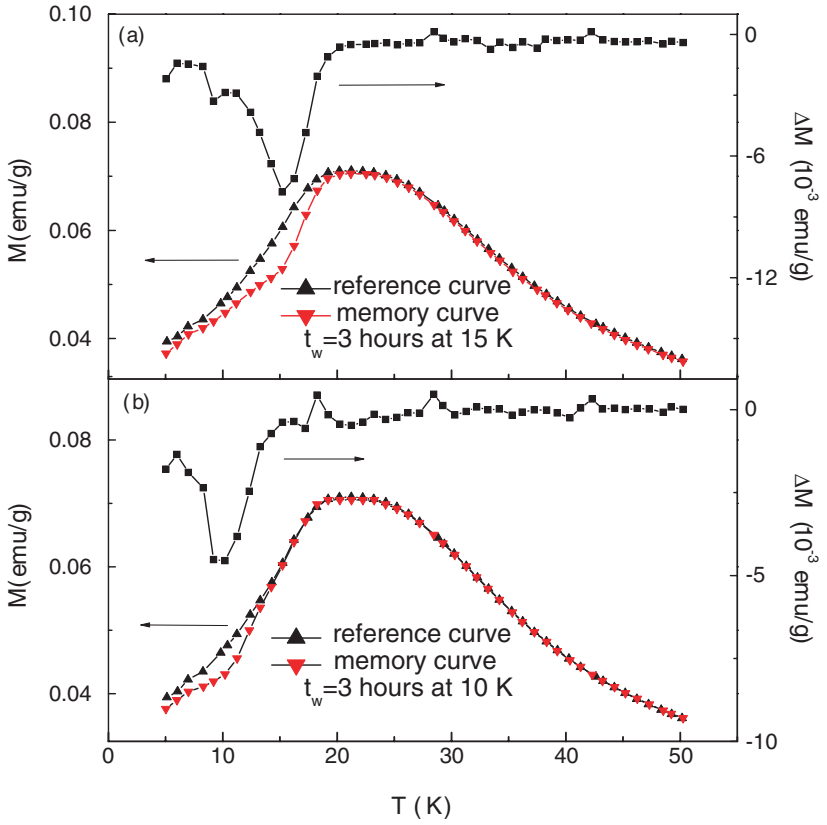

Figure 6. Temperature dependence of the reference magnetization $M_{\rm ref}$, the memory magnetization M, and the difference between them. The reference curve was measured from 5 to 50 K in a 50 Oe field after a zero-field cooling from 300 to 5 K; the memory curve was measured from 5 to 50 K in a 50 Oe field after a zero-field cooling with a halting for 3 h at (a) 15 K and (b) 10 K.

temperatures, which is very similar to that observed in $(La_{0.25}Nd_{0.75})_{0.7}Ca_{0.3}MnO_3$ [7] and $La_{0.82}Sr_{0.18}CoO_3$ [8]. When the dc field reaches 9 T, T_{f2} shifts to 80 K, which implies the existence of magnetic clusters whose sizes increase with increasing applied field in $(La_{0.5}Nd_{0.5})_{1.2}Sr_{1.8}Mn_2O_7$.

The unusual dependence of T_f on the dc magnetic field indicates that both a spin-glass-like phase and an assembly of magnetic clusters contribute to the glassy magnetic behaviour in the system. Such a complex magnetic configuration is probably due to phase separation. There have been plenty of experiments to indicate phase separation in bilayered manganites [2]. In particular, nuclear magnetic resonance and Hall effect measurements suggest a tendency of phase separation at low temperature in $La_{1.2}Sr_{1.8}Mn_2O_7$ [19, 20]. In $(La_{0.5}Nd_{0.5})_{1.2}Sr_{1.8}Mn_2O_7$, substituting La with Nd changes the lattice constants and influences the orbital character of the e_g electrons so that the short-range ordering of charge and orbit might be enhanced. As a result, the tendency of phase separation is enhanced. Thus, it is proposed that $(La_{0.5}Nd_{0.5})_{1.2}Sr_{1.8}Mn_2O_7$ is in a phase-separated state at low temperature in which nanoscale ferromagnetic clusters coexist with the short-range charge/orbital ordered regions. In fact, a similar phase-separation picture has been proposed for $(La_{0.4}Pr_{0.6})_{1.2}Sr_{1.8}Mn_2O_7$ [9]. In such

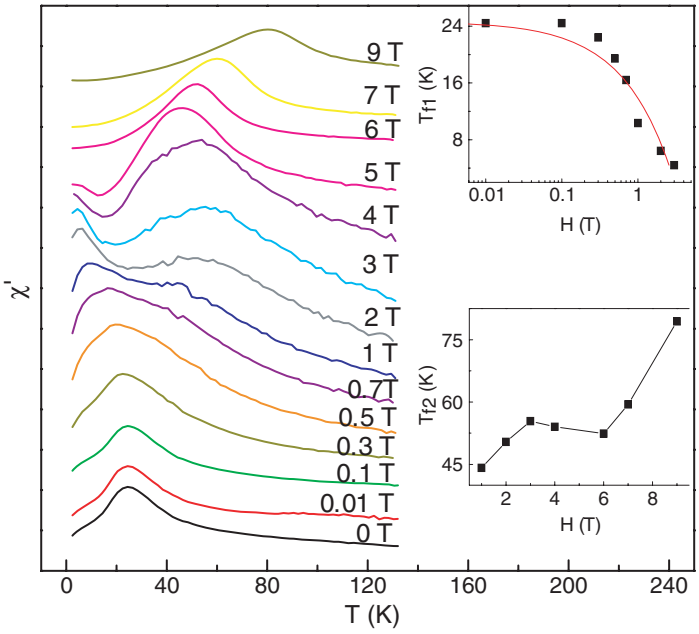

Figure 7. Temperature dependence of ac susceptibility with different superimposed dc fields for $(La_{0.5}Nd_{0.5})_{1.2}Sr_{1.8}Mn_2O_7$ at a frequency of 11 Hz in an ac field of 10 Oe. Upper inset: T_{f1} versus H_{dc}. The solid line is the best fit to an Almeida–Thouless line. Lower inset: T_{f2} versus H_{dc}.

a phase-separated state, as discussed in [8], a spin-glass-like phase may exist at the interface regions between the ferromagnetic clusters and the surrounding matrix. Therefore, both a spin-glass-like phase and an assembly of magnetic clusters may contribute to the glassy magnetic behaviour.

To further study the nature of the glassy magnetic behaviour in bilayered manganites, the magnetic relaxation is measured using the method described in [7]. Ulrich *et al* [21] proposed that in interacting magnetic particles systems, dipolar interactions cause the relaxation rate, $W(t) = -(\mathrm{d}/\mathrm{d}t)\ln M(t)$, to decay by a power law, i.e. $W(t) = At^{-n}$, with an exponent n which depends on the concentration and on the strength of the magnetic interaction. The relaxation experiments were measured in the following sequence: (1) the sample of $(La_{0.5}Nd_{0.5})_{1.2}Sr_{1.8}Mn_2O_7$ was cooled with a 50 Oe magnetic field from 300 K to the temperature T_m continuously at a constant cooling rate of 2 K min^{-1}; (2) after the temperature of T_m became stable, the 50 Oe field was switched off; (3) after waiting for 10 000 s, the magnetization as a function of time $M(t)$ was measured. Figure 8 shows the decay of $W(t)$ and the values of n obtained for different temperatures below 25 K (T_f). n is slightly below 1, suggesting that the intercluster interaction is significant. Analogous to $La_{0.82}Sr_{0.18}CoO_3$ [8], n is not constant and increases continuously as T_f is approached; for example, n is 0.789 for 5 K while n is 0.886 for 20 K. These are opposite to the system for a true spin-glass or strongly interacting particles with fixed diameter and concentration where n is expected to be constant with the increase of temperature. Since n is a parameter reflecting the strength of interaction, the increase of n with temperature indicates the increasing strength of the intercluster interactions as T_f is approached. These results are consistent with the field dependence of the ac susceptibility.

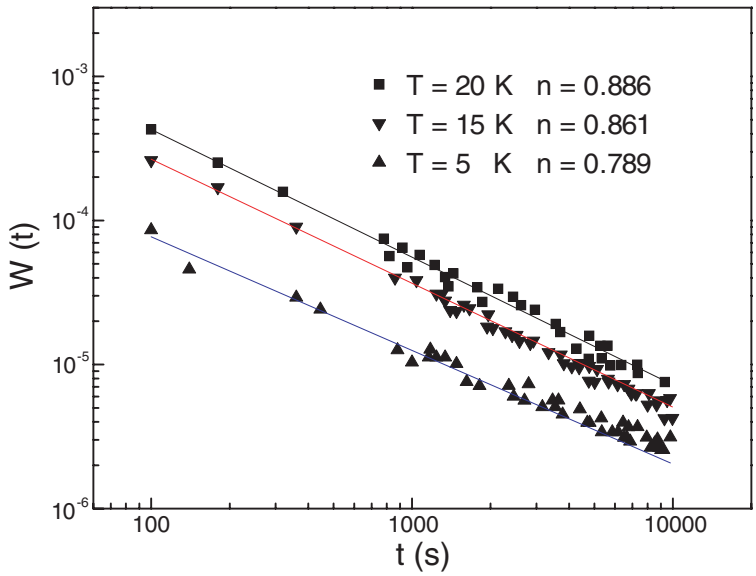

Figure 8. Relaxation rate $W(t) = -(\mathrm{d}/\mathrm{d}t)\ln M(t)$ versus $\log_{10} t$ at different temperatures. The solid lines are the best fits to the function of $W(t) = At^{-n}$.

4. Conclusion

In conclusion, we have studied the glassy magnetic behaviour in a $(La_{0.5}Nd_{0.5})_{1.2}Sr_{1.8}Mn_2O_7$ single crystal. The observed phenomena of frequency dependence of the ac susceptibility as well as ageing and memory effects indicate a 'glassy state' at low temperature. However, there exist two peaks in the ac susceptibility with superposed dc fields. One peak shifts to lower temperatures and another shifts to higher temperatures with increasing field, which suggests that the system is not in a classical spin-glass phase. Instead, based on the picture of phase separation, these results can be understood taking into account both a spin-glass-like phase and an assembly of interacting magnetic clusters. The analysis of the relaxation rate as a function of temperature using a previous model confirms this picture. Therefore, our experiments clarify that the glassy magnetic behaviour in a $(La_{0.5}Nd_{0.5})_{1.2}Sr_{1.8}Mn_2O_7$ single crystal is due to both an assembly of magnetic clusters and a spin-glass-like phase.

Acknowledgments

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