Logarithmic growth law in the two-dimensional Ising spin glass state resulting from the electron doping in single-layered manganites

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The ac-susceptibility of the electron doped single-layered manganite La$_{1.1}$Sr$_{0.9}$MnO$_4$ is analyzed in detail. A quasi two-dimensional (2D) antiferromagnetic (AFM) order with Ising anisotropy is stabilized below $T_N \sim 80$K. We show that below $T_N$, a rare 2D spin-glass (SG) correlation develops with the same Ising anisotropy as the AFM state. Using simple scaling arguments of the droplet model, we derive a scaling form for the ac-susceptibility data of a 2D SG, which our experimental data follows fairly well. Due to simplifications in this 2D case, the proposed scaling form only contains two unknown variables $\psi\nu$ and $\tau$. Hence, the logarithmic growth law of the SG correlation predicted by the droplet model is convincingly evidenced by the scaling of our experimental data. The origin and nature of this 2D SG state is also discussed.

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Depending on the size of the ionic radii of the R$^{3+}$ and A$^{2+}$ ions in the $(R_{1-x}A_x)_{n+1}$Mn$_n$O$_{3n+1}$ manganites (R is a rare earth and A is an alkaline earth element), the ferromagnetic metallic phase, or the charge- and orbital-ordered (CO-OO) can be stabilized[1]. It has been shown in the three-dimensional perovskite case ($n=\infty$, $R_{1-x}A_x$MnO$_3$) that in the presence of the quenched disorder introduced by the solid solution of the $R^{3+}/A^{2+}$ ions, the long-range CO-OO phase collapses in a first-order manner[2], and only a nanometer-sized CO-OO correlation, and associated spin glass (SG) state remains[3]. In the two-dimensional case ($n=1$, $R_{1-x}A_x$MnO$_4$), the short-range CO-OO state, or CE-glass[4], is also observed, albeit the first-order like collapse of the CO-OO does not occur[5]. The associated SG state is atomic-like in both cases[6, 7], as it results of the uniform fragmentation of the ferromagnetic zig-zag chains constituting the CO-OO structure on the nanometer scale[2]. This “orbital-master/spin-slave” relationship is valid for hole-doped manganites with half-doping or larger (0.5 $\leq x < 1$)[8]. However in hole-underdoped manganites, a low-temperature SG state may appear even if the CO-OO is long ranged[9, 10], as magnetic frustration is introduced with the “excess electrons” in the structure.

We here investigate the spin-glass state of electron-doped single-layered manganites (i.e. with $x < 0$). While the undoped LaSrMnO$_4$ ($x=0$) is antiferromagnetic, an uncommon two-dimensional (2D) SG state with Ising anisotropy is observed in the electron doped La$_{1.1}$Sr$_{0.9}$MnO$_4$. Using simple scaling arguments from the so-called droplet model, we derive a simple form of the full dynamical scaling of the temperature- and frequency-dependent ac-susceptibility of such a 2D spin-glass, which is found to describe our experimental data. Due to the great simplification of the scaling form in this 2D case, our scaling analysis convincingly confirms the logarithmic growth law of the spin-glass correlation predicted by the droplet model. The origin of this 2D Ising SG, as well as the relationship between orbital and spin degree of freedom are also discussed.

High quality single crystals of the La$_{1.1}$Sr$_{0.9}$MnO$_4$ were grown by the floating zone method. The phase-purity of the crystals was checked by x-ray diffraction. The ac-susceptibility $\chi(\omega = 2\pi f)$ data was recorded as a function of the temperature $T$ and frequency $f$ on a MPM-SXL SQUID magnetometer equipped with the ultra low-field option (low frequencies) and a PPMS6000 (higher frequencies), after carefully zeroing or compensating the background magnetic fields of the systems. Additional phase corrections were performed for some frequencies. The heat capacity $C$ was recorded using a relaxation method on the same measurement system.

LaSrMnO$_4$ ($x=0$) is an antiferromagnet (AFM) below $T_N \sim 120$K, with the K$_2$NiF$_4$ structure[10, 11]. In these single-layered crystals with the typical lattice-parameter ratio $c/a > 3$, the MnO$_2$ planes (ab-planes) are isolated by blocking (La/Sr)$_2$O$_2$ layers, yielding a 2D Mn−O network which limits the spatial extent of the magnetic and charge- and orbital correlation along the c-axis of the structure. All Mn ions are Jahn-Teller Mn$^{3+}$ ions with three $t_{2g}$ electrons ($d_{xy}, d_{yz},$ and $d_{zx}$ orbitals), and an $e_g$ electron occupying the c-oriented $d_{3z^2-r^2}$ orbital[12]; the last 3d orbital, the ab-oriented $d_{x^2-y^2}$, is unoccupied. As a result, the AFM state shows an Ising anisotropy, with spins parallel to the c-axis of the structure[10, 11]. When electrons are added to
LaSrMnO₄ by increasing the amount of La³⁺ with respect to Sr²⁺, as in La₁₁Sr₀.₉MnO₄, Mn²⁺ ions are created, with both d₃z²−r² and dₓ²−y² orbitals occupied.

As seen in the upper panel of Fig. 1, the in-phase component of ac-susceptibility χ′(ω,T) recorded with a probing magnetic field h applied along the c-axis of the structure, exhibits two overlapping peaks at low temperatures. A sharp peak near 80 K, and a broad peak above 50 K with large frequency dependence, nearly masking the former. Instead, χ′(ω,T) recorded with h within the ab-plane is rather flat below 80K, and frequency independent. Accordingly, the corresponding out-of-phase component, χ″(ω,T) is negligible at all temperatures (see lower panel of Fig. 1). The temperature dependence and anisotropy of χ′(ω,T) are reminiscent of those of an AFM with spins parallel to the c-axis, albeit with a broad frequency dependent peak superposed in the c-direction. The AFM transition is confirmed by heat capacity measurements, as seen in Fig. 2. Below T_N, the heat capacity only exhibit a broad feature, which may reflect magnetic disorder or glassiness at low temperatures [13].

The low-temperature broad peak observed in the χ′(ω,T) displays the same Ising anisotropy as the AFM state, and χ′(ω,T) recorded with h//c resembles that of SG or superparamagnets [3, 14]. The additional e_g electrons in Mn²⁺ are likely to hop onto neighboring empty e_g states and host the ferromagnetic (FM) interaction by double-exchange mechanism [1], yielding the appearance of FM correlation in the original AFM structure of LaSrMnO₄. Hence a reentrant SG state, or a superparamagnetic state might appear in La₁₁Sr₀.₉MnO₄. The Hund coupling on Mn²⁺ sites align the spins of the e_g and t₂g orbitals along the c-axis, yielding the observed Ising anisotropy of the low-temperature disordered state.

We now study the time and frequency dependence of the ac-susceptibility in more detail, in order to determine the nature of the low-temperature state. Because of the Ising anisotropy, the probing ac magnetic field is applied along the c-axis. Three-dimensional (3D) SG states have frequently been observed in similar single-layered [5, 6, 9], as well as in pseudo-cubic perovskite [3] manganites doped with holes. It could thus be expected that a similar SG state appears in the present electron-doped case. As seen in the lower inset of Fig. 1, La₁₁Sr₀.₉MnO₄ displays aging features characteristic of spin glasses [3, 14, 15], reflecting the slow rearrangement of the spin configuration toward its equilibrium state at a given temperature within the glassy phase after a quench to that temperature [15].

In each χ''(ω,T) curve in the lower panel of Fig. 1, we can define a frequency dependent freezing temperature T_f(f), below which the system is out-of-equilibrium (typically the temperature onset of χ''(ω,T), see below). In each measurement, the system is probed on a typical time scale τ_obs ~ 1/ω (ω = 1/2πf) or a length scale L(1/ω). One can check whether the dynamical slowing down toward the SG phase transition occurs by scaling τ_obs = τ(T_f) with the reduced temperature ε = (T_f(T) − T_g)/T_g (T_g is the spin glass phase transition temperature) using the power law form [3, 14, 15]:

\[
\frac{\tau}{\tau_0} = \epsilon^{-z\nu}
\]

where z and ν are critical exponents, and τ₀ the flip-
The dynamical exponent $F$ fails equally (and $\tau_0 > 10^{-19}$ s), implying that our data does not reflect the superparamagnetic relaxation. Due to the simple Arrhenius law relating $T_f$ and $t_{obs}$, the superparamagnetic relaxation implies for $\chi''(\omega,T)$: $\chi'' = F(\log(T/T_0))$ where $F$ is a numerical function. The scaling of our experimental data using this scaling form fails (which can be expected as the magnitude of the maximum of $\chi''(\omega,T)$ depends on the frequency), and yields unphysical $\tau_0$ values, as in the case of the simple $T_f(f)$ scalings.

We now check whether the disordered state observed at low temperatures in La$_{1.1}$Sr$_{0.9}$MnO$_4$ behaves like a 2D SG, i.e. with 2D SG correlation developing below $T_N$. In that case, the dynamical slowing down is expressed with the generalized Arrhenius law ($T_g=0$):

$$\log\left(\frac{\tau}{\tau_0}\right) \propto \frac{1}{T_f(f)^{1+\psi\nu}}$$

where $\psi$ is the energy barrier exponent. As shown in the inset of Fig. 1, the scaling of the $T_f(f)$ data works fairly well, with meaningful values for $\psi\nu$ and $\tau_0$. The obtained value of $\tau_0 \sim 10^{-12\pm 1}$ s is close to the microscopic spin flipping time which indicates that the SG state is nearly atomic, with fluctuating entities of the nanometer order. The dynamical exponent $\psi\nu$ value of 0.8 ± 0.1 is reasonably smaller than 1[17], and similar to those of other 2D systems. Using a similar analysis, $\psi\nu \sim 0.9$ was obtained in (Cu,Mn)/Cu multilayers with 2D SG character[17], while $\psi\nu \sim 1.5$ was obtained for B$_{12}$ cluster compound HoB$_{22}$C$_2$N[14]. Hence the low-temperature state La$_{1.1}$Sr$_{0.9}$MnO$_4$ seems to behave like

![Figure 3](image-url)  
**FIG. 3:** (Color online) Temperature dependence of the in-phase (upper panel) and out-of-phase (lower panel) components of the ac-susceptibility $\chi''(T,\omega)$ and $\chi'(T,\omega)$ for different frequencies. The probing field is applied along the $c$-direction. The inset shows the relaxation of $\chi''(T,\omega)$ as a function of time $t$ after a quench from high temperatures.

![Figure 4](image-url)  
**FIG. 4:** (Color online) Full scaling of the $\chi''(T,\omega)$ curves using the scaling law derived in the main text. $\psi$ and $\nu$ are critical exponents while $\tau_0$ reflects the flipping time of the fluctuating entities. The inset shows the scaling of the observation time $\tau = 1/\omega$ (as $\log(\tau)$) with $1/T_f^{1+\psi\nu}$; $T_f(\omega)$ is the frequency dependent freezing temperature.
a 2D SG. However, as in the previous 3D and superparamagnetic \( T_f(f) \) scalings, \( T_f \) may not be accurately defined, and we need to perform a full scaling analysis. For that purpose, we derive a scaling form \( [20] \) for the dynamical slowing down in a 2D SG, based on the droplet picture.

The generalized Arrhenius law mentioned above stems from the droplet model \( [13] \), and the fact that thermal activation over energy barriers \( L^\nu \) for a droplet excitation of length \( L \) implies the logarithmic growth \( [17, 18] \):

\[
L \propto (T \log(t))^{1/\psi}
\]

This thus implies that \( L \) compares to the correlation length \( \xi \) as:

\[
\frac{L}{\xi} \propto \left( \frac{T \log(t)}{\xi^\psi} \right)^{1/\psi}
\]

\[
T \log(t) \frac{q(t)}{\xi^\psi}
\]

is thus the natural scaling variable for the spin autocorrelation function \( q(t) \) \( [23] \), as:

\[
q(t) = t^{-x} F \left( \frac{T \log(t)}{\xi^\psi} \right)
\]

\( F \) is a functional form and \( x \) an exponent. In two dimensions, \( T_\beta=0 \), \( x=\frac{1}{2} (d-2+\eta)=0 \) and \( \xi \) diverges as \( T^{-\nu} \), yielding the fairly simple form:

\[
q(t) = F(T^{1+\nu} \log(t/t_0))
\]

\( q(t) \) is related to the time dependent zero-field susceptibility \( \chi(t) \) and the experimental susceptibility \( \chi(\omega, T) \) by the fluctuation-dissipation theorem as:

\[
\chi(t) = \frac{1-q(t)}{T^2 \log(t/t_0)} \quad \text{and} \quad \chi' = -\frac{d\chi(t)}{d \log(t)}.
\]

Hence combining these expressions, we can write:

\[
\chi''(\omega = 2\pi f, T) = \frac{2 T^{\nu} F'(2+\nu) \log(t/t_0)}{T^{2+\nu} \log(t/t_0)}
\]

which can be rewritten, using \( G=F' \):

\[
\chi''(2\pi f, T) T^{\nu} = G(-T^{1+\nu} \log(2\pi T f))
\]

This scaling form is quite simple, with only two parameters \( \psi \) and \( \tau_0 \), due to the above mentioned simplifications in the 2D case. Our experimental \( \chi''(\omega, T) \) data is analyzed using this scaling form. As seen in the main panel of Fig. 4 a fairly good scaling of the different \( \chi''(\omega, T) \) curves can be obtained if plotted using the above derived scaling law. The scaling implies \( \psi=0.9 \pm 0.1 \) and \( \tau_0 = 10^{-11} \) s, in agreement with the \( T_f(f) \) scalings. If we assume that \( \nu = -1/\theta \sim 3.5 (\theta \sim -0.29) \) \( [27] \), we obtain \( \psi=0.26 \), in agreement with theoretical predictions \( [27] \).

Hence we suggest that as the temperature is lowered below \( T_N \), a 2D SG correlation develops in \( \text{La}_1.1 \text{Sr}_{0.9} \text{MnO}_4 \). The 2D character may be related to the \( d_{x^2-y^2} \) orbital nature of the electrons injected in the single-layered structure. In this layer case, the interplanar interaction is further weakened by the interplane frustration \( [11, 23] \), which implies that the AFM state established in \( \text{LaSrMnO}_4 \) and \( \text{La}_{1.1} \text{Sr}_{0.9} \text{MnO}_4 \) is quasi 2D. The introduction of additional \( \epsilon_f \) electrons in the latter introduces the local FM interaction responsible for the 2D SG correlation with Ising anisotropy inherited from the long-ranged AFM state stabilized at higher temperatures.

To conclude, we have investigated in detail the ac-susceptibility of the electron-doped \( \text{La}_{1.1} \text{Sr}_{0.9} \text{MnO}_4 \) single-layered manganite. We have evidenced the appearance of an uncommon two-dimensional spin-glass correlation at low temperatures, as a result of the appearance of ferromagnetic interaction in the quasi two-dimensional antiferromagnetic state of \( \text{LaSrMnO}_4 \) promoted by the electron doping. Using simple scaling arguments of the droplet model, we have derived a scaling form describing the dynamical scaling of the ac-susceptibility of such a two-dimensional spin-glass state. A good scaling of the experimental data is obtained using this scaling form, confirming the two-dimensional nature of the low-temperature spin-glass state of \( \text{La}_{1.1} \text{Sr}_{0.9} \text{MnO}_4 \). Because of great simplifications in two dimension, the scaling form involves only two free parameters, so that the scaling of our experimental data convincingly confirm the validity of the scaling form, and thus the logarithmic growth law of the droplet model.

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\[ \text{[2] Y. Tokura and N. Nagaosa, Science } 288, 462 (2000). \]

\[ \text{[3] Y. Tomioka and Y. Tokura, Phys. Rev. B 70, 014432 (2004).} \]

\[ \text{[4] R. Mathieu, D. Akahoshi, A. Asamitsu, Y. Tomioka, and Y. Tokura, Phys. Rev. Lett. 93, 227202 (2004).} \]

\[ \text{[5] R. Mathieu, D. Magnoux, A. Moreo, D. Poilblanc, S. Yunoki, and E. Dagotto, Phys. Rev. B 68, 104405 (2003).} \]

\[ \text{[6] R. Mathieu, M. Uchida, Y. Kaneko, J. P. He, X. Z. Yu, R. Kumai, T. Arima, Y. Tomioka, A. Asamitsu, Y. Matsui, and Y. Tokura, Phys. Rev. B 74, 020404(R) (2006).} \]

\[ \text{[7] R. Mathieu, A. Asamitsu, Y. Kaneko, J. P. He, and Y. Tokura, Phys. Rev. B 72, 014436 (2005).} \]

\[ \text{[8] D. Akahoshi, M. Uchida, T. Arima, Y. Tomioka, and Y. Tokura, Phys. Rev. B 74, 012402 (2006).} \]

\[ \text{[9] X. Z. Yu, R. Mathieu, T. Arima, Y. Kaneko, J. P. He, M. Uchida, T. Asaka, T. Nagai, K. Kimoto, A. Asamitsu, Y. Matsui, and Y. Tokura, Phys. Rev. B 75, 174441 (2007).} \]

\[ \text{[10] R. Mathieu, J. P. He, X. Z. Yu, Y. Kaneko, M. Uchida, Y. S. Lee, T. Arima, A. Asamitsu, and Y. Tokura, cond-mat/0701191.} \]

\[ \text{[11] S. Larochelle, A. Mehta, L. Lu, P. K. Mang, O. P. Vajk,}\]
[5] N. Kaneko, J. W. Lynn, L. Zhou, and M. Greven, Phys. Rev. B 71, 024435 (2005).
[11] Y. Moritomo, Y. Tomioka, A. Asamitsu, Y. Tokura, and Y. Matsui, Phys. Rev. B 51, R3297 (1995).
[12] J. v. Elp, H. Sato, T. Kimura, T. Toda, Y. Okamura, Y. Tokura, and M. Taniguchi, J. Phys. Soc. Jpn 69, 2391 (2000).
[13] G. E. Brodale, R. A. Fisher, W. E. Fogle, N. E. Phillips, and J. v. Curen, J. Magn. Magn. Mater. 31-34, 1331 (1983).
[14] M. F. Hansen, P. E. Jönsson, P. Nordblad, and P. Svedlindh, J. Phys.: Condens. Matter 14, 4901 (2002).
[15] P. E. Jönsson, R. Mathieu, P. Nordblad, H. Yoshino, H. Aruga Katori, and A. Ito, Phys. Rev. B 70, 174402 (2004).
[16] T. Jonsson, J. Mattsson, P. Nordblad, and P. Svedlindh, J. Magn. Magn. Mater. 168, 269 (1997).
[17] C. Djurberg, J. Mattsson, P. Nordblad, L. Haines, and J. A. Cowen, J. Magn. Magn. Mater. 140-144, 1721 (1995).
[18] D. Fisher and D. Huse, Phys. Rev. B 36, 8937 (1987); Phys. Rev. B 38, 386 (1988).
[19] T. Mori and H. Mamiya, Phys. Rev. B 68, 214422 (2003).
[20] One such scaling form has been proposed in Ref. [21]. However, the steps yielding its derivation are unclear, and involve the critical exponent $\gamma$, which implies a large dependence ($\sim T^\gamma$) on the frequency of the magnitude of the maximum of $\chi''(\omega, T)$. Such a large dependence is not observed in our system, nor in the other known 2D systems mentioned in the main text. See [10] [22].
[21] C. Dekker, A. F. M. Arts, H. W. de Wijn, A. J. v. Duyn-eveilt, and J. A. Mydosh, Phys. Rev. B 40, 11243 (1989).
[22] P. Granberg, P. Nordblad, P. Svedlindh, L. Lundgren, R. Stubi, G. G. Kenning, D. L. Leslie-Pelecky, J. Bass, and J. Cowen, J. Appl. Phys. 67, 5252 (1990).
[23] D. S. Fisher, J. Appl. Phys. 61, 3672 (1987).
[24] L. Lundgren, P. Svedlindh and O. Beckman, J. Magn. Magn. Mater. 25, 33 (1981).
[25] S. Onoda, Y. Motome, and N. Nagaosa, Phys. Rev. Lett. 92, 236403 (2004).
[26] J. Kisker, L. Santen, M. Schreckenberg, and H. Rieger, Phys. Rev. B 53, 6418 (1996).
[27] C. Amoruso, A. K. Hartmann, and M. A. Moore, Phys. Rev. B 73, 184405 (2006); A. K. Hartmann, A. J. Bray, A. C. Carter, M. A. Moore, and A. P. Young, ibid. 66, 224401 (2002); see also H. G. Katzgraber, L. W. Lee, and A. P. Young, Phys. Rev. B 70, 014417 (2004).