Spin-glass behavior in $La(Fe_{1-x}Mn_x)_{11.4}Si_{1.6}$ compounds

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The magnetic properties of $La(Fe_{1-x}Mn_x)_{11.4}Si_{1.6}$ ($0 \leqslant x \leqslant 0.08$) compounds were investigated. A reentrant spin glass behavior for the sample with $x=0.06$ and a paramagnetic-to-spin glass transition for the sample with $x=0.08$ were observed. The spin-glass behavior for the sample with $x=0.08$ was systematically studied by the dc and ac measurements. $\Delta T_f(\omega)/[T_f(\omega)\Delta \log_{10}\omega]$, a possible distinguishing criterion to assert the presence of a spin-glass phase was 0.02 for the sample with $x=0.08$. The frequency-dependent data turned out to be well described by the conventional critical slowing down law $\tau/\tau_0=\varepsilon^{-zv}$. The fit to this critical slowing down law yielded the values $\tau_0=10^{-12}$ s, $zv=8.28$, and the transition temperature $T_{SG}=45.24$ K. This spin-glass behavior in $La(Fe_{1-x}Mn_x)_{11.4}Si_{1.6}$ compounds is mainly ascribed to the competing interaction between the Fe-Fe ferromagnetic ordering and the Fe-Mn, Mn-Mn antiferromagnetic ordering.

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I. INTRODUCTION

Extensive attention has been paid to the magnetic properties of $NaZn_{13}$-type $LaFe_{13-x}Si_x$ compounds. They exhibit a first-order magnetic phase transition near the Curie temperature, as well as an itinerant-electron metamagnetic (IEM) transition.[1–3] The IEM transition brings about a very large magnetic entropy change for the compounds with $x \leqslant 1.6$.[4,5] Previous research results confirmed that the addition of a small amount of Mn will bring about obvious changes in the magnetic properties and magnetic entropy change of $LaFe_{13-x}Si_x$ compounds.[6] In the present work, we focus on the effects of Mn on the magnetic properties in $La(Fe_{1-x}Mn_x)_{11.4}Si_{1.6}$ compounds. A spin-glass behavior is first observed in $La(Fe_{1-x}Mn_x)_{11.4}Si_{1.6}$ compounds when the Mn content exceeds ~0.06. Here we give the main results of our study.

II. EXPERIMENT

The detailed preparation of $La(Fe_{1-x}Mn_x)_{11.4}Si_{1.6}$ compounds ($x=0$, 0.02, 0.04, 0.06, and 0.08) can be found elsewhere.[6] Powder x-ray diffraction (Cu $K\alpha$) patterns revealed that all the samples crystallize in a single phase with the cubic $NaZn_{13}$-type structure ($Fm3c$) at room temperature and the lattice constant increases slightly with the increase of the Mn concentration, which is due to the larger atomic radius of the Mn atoms than that of Fe ones. All the magnetic measurements were performed on a superconducting quantum interference device (SQUID) magnetometer and a physical property measurement system.

III. RESULTS AND DISCUSSION

The temperature dependence of zero-field-cooled (ZFC) and field-cooled (FC) magnetizations measured under an applied field of 0.01 T are shown in Fig. 1. A simple paramagnetic-(PM-) ferromagnetic (FM) transition is observed in the samples with $x \leqslant 0.04$ at Curie temperature, which monotonously decreases with increasing Mn content. For the sample with $x=0.06$, however, the $M(T)$ curve displays two transitions: a PM-FM transition and a FM spin-glass (SG) transition at 100 and 21 K. This PM-FM-SG transition is called a reentrant spin glass (RSG).[7] While a PM-SG transition appears at about 46 K for the sample with $x=0.08$, which is evidenced by a cusp in the ZFC curve and a distinctive separation of the FC and ZFC curves.[8]

To exclude the existence of ferromagnetic or other long-range ordering, $M(H)$ under the ZFC condition for the sample with $x=0.08$ was also measured up to 5 T at temperatures between 5 and 120 K. And Arrott plots of magnetization, a plot of the square of the magnetization M as a function of H/M, were constructed,[9] as shown in Fig. 2. The data taken at high fields are fitted by straight lines. The Arrott plots show no positive intercepts at any temperature, which confirms that there is no long-range order at all for the sample with $x=0.08$.[10]

Figure 3 shows the isothermal magnetization curves for all the samples at 5 K. It shows an obvious decrease of the magnetization with the increase of x, and the full saturation state is not achieved even under a field of 5 T for the samples with $x=0.06$ and 0.08, indicating that no true long-range

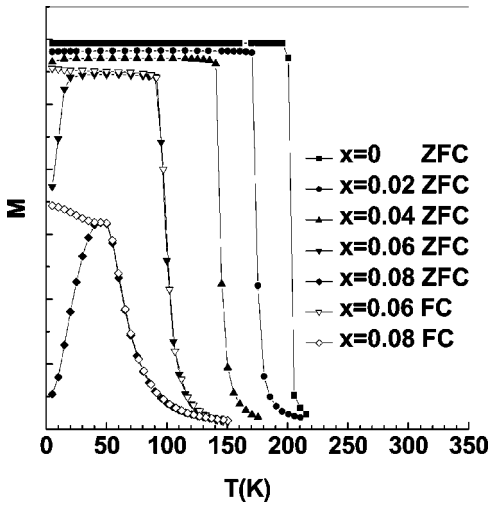


FIG. 1. Temperature dependence of magnetization for $La(Fe_{1-x}Mn_x)_{11.4}Si_{1.6}$ compounds ($x=0$,0.02,0.04,0.06,0.08) under a low magnetic field of 0.01 T by ZFC and by FC only for the samples with $x=0.06$ and $x=0.08$.

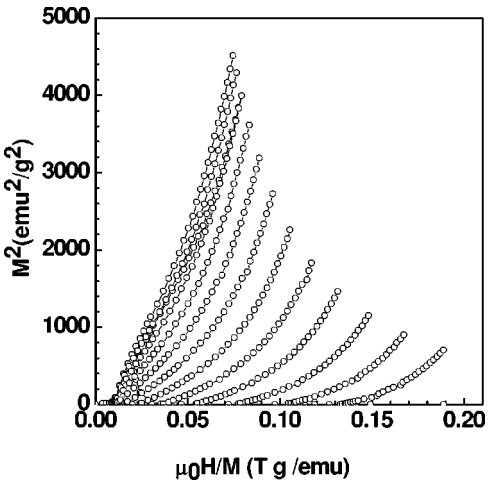


FIG. 2. Arrott plots of magnetization at different temperatures between 5 and 120 K for the sample with $x=0.08$.

order exits. Furthermore an S-shaped curve characteristic of SG systems has been obtained for the sample with $x=0.08$. Figure 4 shows the temperature dependence of coercive field H_c and remanent magnetization M_r data obtained from the ZFC hysteresis loops for the sample with $x=0.08$ at different temperatures. Both H_c and M_r increase with lowering temperature below the SG freezing temperature T_f, which is in accordance with that observed in other spin-glass system.[8] The fact that it is hard to saturate the $M(H)$ curve and the large separation between the FC and ZFC curves, the existence of the hysteresis and large coercivity at low temperatures indicate the SG characters for sample $x=0.08$. Hereafter, we mainly discuss the spin-glass behavior of the sample with $x=0.08$.

In order to understand more the spin-glass behavior of sample with $x=0.08$, we studied its dynamics by ac susceptibility measurement which cover observation time $(1/\omega)$ ranging from 0.1 to 10^{-4} s. Figure 5(a) shows the temperature dependence of the real (χ') component of the ac susceptibility under different frequencies ranging from 10 to 10 000 Hz. The $\chi'(T)$ curve displays a peak at the spin glass transition temperature $T_f(\omega)$, which is frequency dependent. The peak temperature $T_f(\omega)$ shifts towards higher temperatures and the height of the susceptibility peak diminishes with increasing frequency. The value of the frequency sensi-

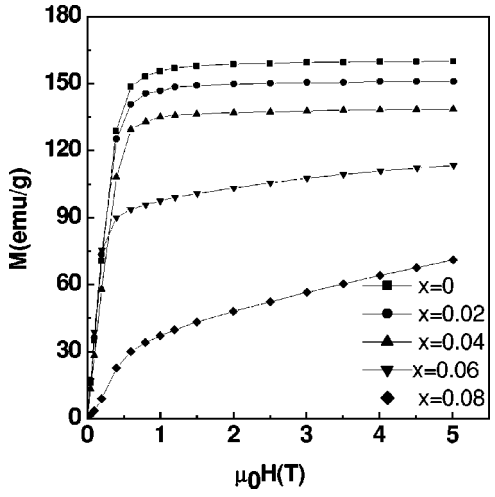


FIG. 3. Magnetic field dependence of magnetization for $La(Fe_{1-x}Mn_x)_{11.4}Si_{1.6}$ compounds ($x=0,0.02,0.04,0.06,0.08$) at 5 K samples.

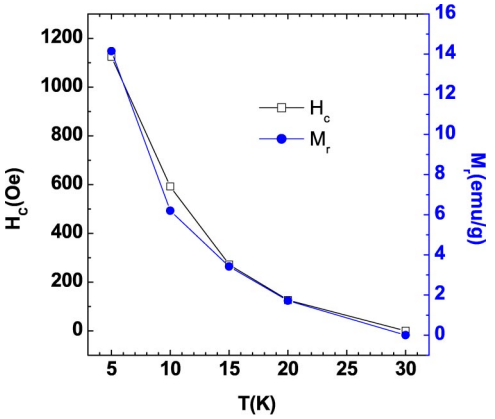
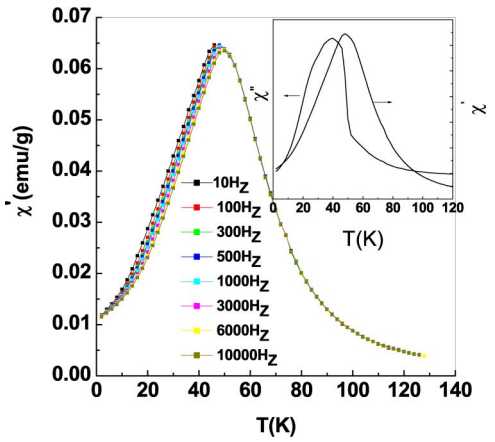


FIG. 4. The temperature dependence of remanent magnetization M_r and coercive field H_c for the sample with $x=0.08$.



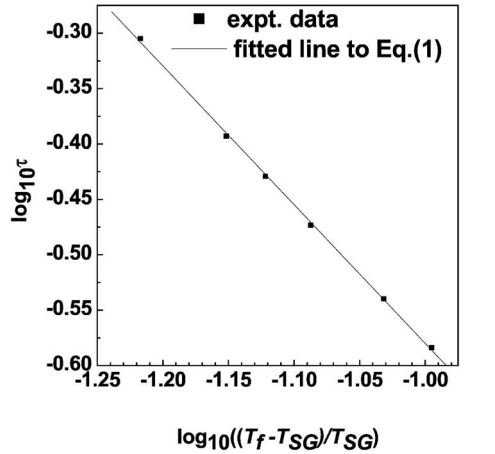


FIG. 5. (a) The temperature dependence of the real (x') part of the ac susceptibility under different frequencies from 10 to 10000 Hz. The inset displays the imaginary χ' and real part χ' of the ac susceptibility measured at 1 kHz. (b) The measured freezing temperature $T_f(\omega)$ and the best fitted line by Eq. (1).

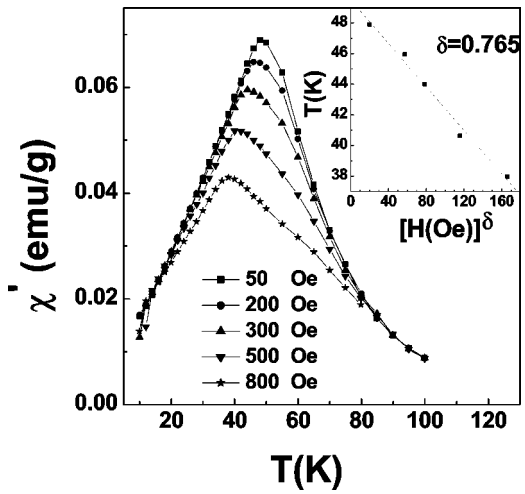


FIG. 6. The temperature dependence of the ac susceptibility measured at a frequency of 10 Hz under different applied dc fields. The inset is the experimental $T_f(H)$ value and the fitted data to Eq. (2).

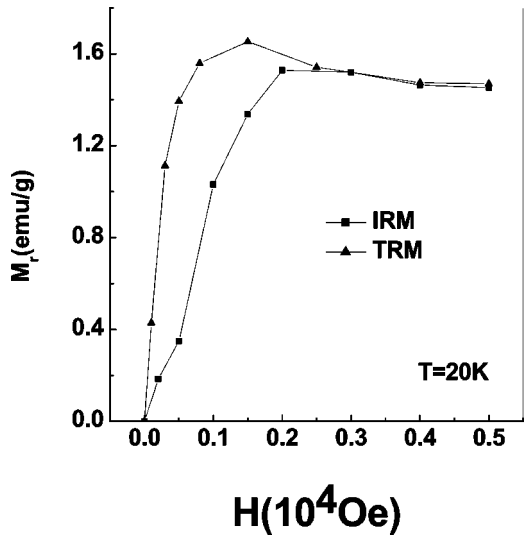


FIG. 7. Remanent magnetization M_r (TRM and IRM) as a function of the applied field.

tivity of $T_f(\omega)$, $\Delta T_f(\omega)/[T_f(\omega)\Delta \log_{10}\omega]$, has been used as a possible distinguishing criterion for the presence of a spin-glass phase. It is 0.02 for the sample with $x=0.08$, very close to that of the conventional spin glasses.[11] The imaginary χ' and real part χ' of the ac susceptibility measured at 1 kHz is presented as a function of temperature in the inset of Fig. 5(a). χ'' also exhibits a peak at ~40 K and a sudden fall near T_f. The peak is not very sharp indicating that some small ferromagnetic clusters are formed. However, no true long-range order exits.

The divergence of the maximum relaxation time $\tau_{\max}$, occurring at the spin-glass transition temperature, can be investigated by using conventional critical slowing down:

$$\frac{\tau_{\max}}{\tau_0}=\xi^{-zv}=\left(\frac{T_f(\omega)-T_{\mathrm{SG}}}{T_{\mathrm{SG}}}\right)^{-zv}. \tag{1}$$

Here, zv is the dynamic exponent and τ_0 is a microscopic relaxation time. T_{SG} is the spin-glass transition temperature. A best fit of the measured data to Eq. (1) is shown in Fig. 5(b), yielding the values $\tau_0=10^{-12}$ s, $zv=8.28$, and the transition temperature $T_{\mathrm{SG}}=45.24$ K. Both values of τ_0 and zv are the typical values for conventional spin glasses.[12–14] The dynamic scaling, therefore, indicates that there is a divergence of the spin-glass relaxation time at a finite transition temperature, which demonstrates a true phase transition from PM to SG for the sample with $x=0.08$.

One of the characteristic features of a spin glass is the occurrence of sharp cusps in the ac susceptibilities and they are strongly affected by the application of the external field: they smear out and shift downwards.[15] The temperature dependence of the ac susceptibility (the real part) under different applied dc fields measured at a frequency of 10 Hz is displayed in Fig. 6. A peak was observed at about 46 K when the applied field is low. This peak, however, becomes a more rounded maximum by an increase of the external field. Furthermore, both the peak height and the peak temperature decrease with increasing applied field. We have found that the dc field dependence of the freezing temperature $T_f(H)$ follows the equation

$$T_f(H)\propto 1-bH^{\delta}. \tag{2}$$

The inset of Fig. 6 plots the experimental $T_f(H)$ value and the fitted data to Eq. (2). The fitted value of the exponent δ is 0.765. For SG, the mean-field theory predicts $\delta=2/3$. However, this is only a necessary (but not a sufficient) feature of a SG transition.[16] Low dc field magnetization measurements also confirmed the results obtained by the ac susceptibility measurements.

The time response of dc magnetization is important to reveal the spin dynamics for spin-glass systems.[17] The isothermal remanence magnetization (IRM) and thermoremanence magnetization (TRM) for the sample with $x=0.08$ were measured.

The IRM was measured as follows: first the sample was cooled down in zero field from 150 K (well above the spin-glass transition temperature) to 20 K, a magnetic field H was applied for 1 min, then the field was removed and the remanence (IRM) was measured as a function of time. The TRM was measured by cooling the sample in an applied field H from 150 to 20 K, switching off the applied field and measuring the TRM as a function of time.

It was observed that the remanent magnetization is dependent on magnetic history, with $\mathrm{IRM}(H,T)<\mathrm{TRM}(H,T)$ for small fields, as shown in Fig. 7. While in high enough fields, both IRM and TRM saturate to the same value. The field dependence of the TRM and IRM data is quite similar to that of classical spin glasses, such as $Eu_{0.30}Sr_{0.70}S$.[18]

We also measured TRM for different waiting times (500 and 3000 s) at 20 K. The results show that there is a pronounced waiting time dependence of the relaxation. Various functional forms have been proposed to describe the magnetization as a function of observation time and waiting time. One of the most popular relations is the stretched exponential

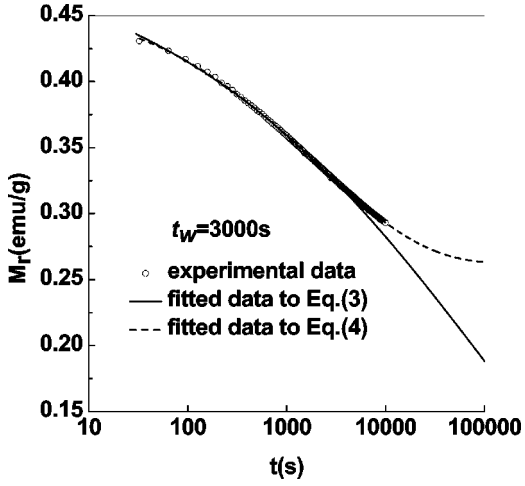


FIG. 8. The best fit of the experimental data measured at $t_w = 3000$ s to Eqs. (3) and (4).

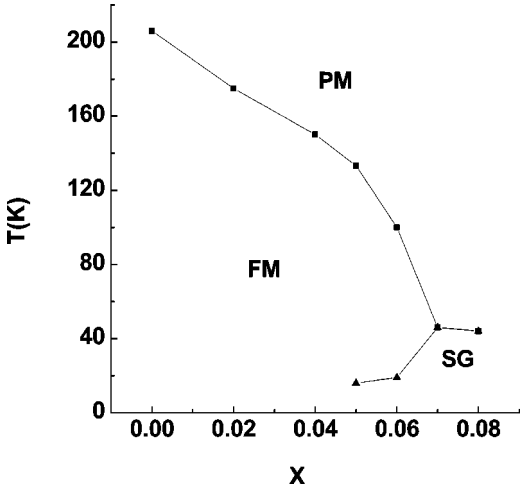


FIG. 9. Phase diagram of temperature versus Mn content (x) for $La(Fe_{1-x}Mn_x)_{11.4}Si_{1.6}$ compounds.

$$M(t) = M_0 \exp[-(t/t_p)^{1-n}], \quad (3)$$

where M_0 and t_p depend on T and t_w, while n is only a function of T.[19] In our cases, however, the stretched exponential function is insufficient to match the data over the whole time interval measured. Nordblad *et al.* found that the total relaxation of the magnetization in CuMn may be described accurately by empirically assuming a pure logarithmic decay superimposed by a stretched exponential form that accounts for the influence of the aging process[20]

$$M_R = SH\ln(t) + M1 + M_{a0}(T,t_w)\exp[-(t/t_p)^{1-n}]. \quad (4)$$

The experimental data measured at $t_w = 3000$ s and the fitted data using Eqs. (3) and (4) are plotted in Fig. 8. One can see that a pure stretched exponential decay is only obtained in limited time intervals around t_w and fitting is greatly improved using Eq. (4) as illustrated by the dashed line in the figure. The parameters obtained from this fitting are $S = 0.46\% M_{FC}/H$, $M_1 = 21\% M_{FC}$, $t_p = 2010$ and $n = 0.48$, and they are in good agreement with those obtained in CuMn spin glasses.

Based on the magnetic data described above, we construct a schematic magnetic phase diagram for the compounds $La(Fe_{1-x}Mn_x)_{11.4}Si_{1.6}$ ($0 \leqslant x \leqslant 0.08$), as shown in Fig. 9. In an ideal $LaFe_{13}$ compound, each Fe_I atom is surrounded by 12 Fe_{II} atoms which build up an icosahedron. Each Fe_{II} atom has 1 Fe_I and 9 Fe_{II} as the nearest neighbors. The change in the coordination number of Fe atoms will cause obvious changes in the magnetic properties.

In $La(Fe_{1-x}Mn_x)_{11.4}Si_{1.6}$ compounds, the Fe-Fe interaction is ferromagnetic, while the Mn-Mn atoms and Fe-Mn atoms couple antiparallelly.[6] The random substitution of Mn for Fe and the competition between the FM and AFM interactions will cause the frustration leading to the spin-glass behavior. In the low Mn concentration, the AFM percentage is low and the long-range FM order still exists, therefore FM behavior is observed for the samples with $x \leqslant 0.04$. With further increasing the Mn concentration, the AFM interaction is comparable to the FM interaction, which will cause large frustration, and finally no long-range ordering exists. In the intermediate Mn concentration region, the RSG behavior is observed.

IV. CONCLUSIONS

Magnetic properties of $La(Fe_{1-x}Mn_x)_{11.4}Si_{1.6}$ ($0 \leqslant x \leqslant 0.08$) compounds have been studied. With increasing Mn concentration, a spin-glass behavior was observed when the Mn content exceeds ~0.06. All the ac and dc magnetic measurements confirm this conclusion. $\Delta T_f/(T_f \Delta \log_{10} f)$, a possible distinguishing criterion to assert the presence of a spin-glass phase, is 0.02 for the sample with $x = 0.08$. The frequency-dependent data turn out to be well described by conventional critical slowing down law $\tau/\tau_0 = \varepsilon^{-zv}$. The values $\tau_0 = 10^{-12}$ s, $zv = 8.28$, and the transition temperature $T_{SG} = 45.24$ K were obtained by fitting the experimental data using critical slowing down law. All the values of $\Delta T_f/(T_f \Delta \log_{10} f)$, τ_0, and zv are very similar to those of the typical spin glasses. The SG state is mainly a result of the competing interaction between the Fe-Fe ferromagnetic ordering and the Fe-Mn, Mn-Mn antiferromagnetic ordering.

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