Spin-glass behavior in hexagonal Na$_{0.70}$MnO$_2$

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(Received 13 October 2006; revised manuscript received 2 February 2007; published 23 March 2007)

In this paper, we present an experimental study of the hexagonal compound Na$_{0.70}$MnO$_2$. Zero-field-cooled and field-cooled susceptibilities display divergences at low temperatures, and the magnetic measurements of frequency dependence of ac susceptibility, hysteresis effect, and long-time relaxation are performed, indicating that Na$_{0.70}$MnO$_2$ undergoes a spin-glass transition at $T_f = 39$ K. The spin-glass order parameter $q(T)$ determined from the dc spin susceptibility exhibits the relation $q(T) \propto (1-T/T_f)$, in agreement with the prediction of conventional spin-glass theory. Spin dynamics in the spin-glass state is carefully examined, and the time decay of the thermoremanent magnetization can be well scaled with a reduced effective waiting time $\lambda/T_f$. The magnetic entropy extracted from the specific heat implies that the spin degrees of freedom of Mn$^{3+}$/Mn$^{4+}$ ions are completely frozen at low temperatures, and the origin of this spin-glass behavior is attributed to the mixture of Mn$^{3+}$/Mn$^{4+}$ ions and geometrical frustrations on the triangular lattices. Comparisons with the magnetic properties of Na$_{0.70}$CoO$_2$ are also made.

DOI: 10.1103/PhysRevB.75.125115

PACS number(s): 71.27.+a, 75.50.Lk, 75.47.Lx

INTRODUCTION

In the last two decades, triangular lattice antiferromagnets have attracted considerable attention due to their rich quantum phenomena. The triangular arrangements of magnetic moments with each pair coupled antiferromagnetically tend to hinder the system to find a unique ground state, i.e., the geometrical frustration. Among them, Na$_x$CoO$_2$ has enjoyed intense studies in recent years. Superconductivity with transition temperature $T_c = 4$ K was observed in the hydrated compound Na$_x$CoO$_2$·yH$_2$O ($x = 0.30, y = 1.3$), while large thermopower and low electrical resistivity coexist in the unhydrated compound Na$_x$CoO$_2$ for $x = 0.7$. Unexpectedly, an insulating state at $x = 0.50$ was observed, involving charge ordering and Na superstructure lattice. The interactions of sodium ions with the underlying cobalt lattice in both hydrated and unhydrated Na$_x$CoO$_2$ give rise to a wide range of possible structure-property relationship. The consequences of strong Coulomb repulsion with geometrical frustration are being intensively investigated.

Experiments have shown large electron-electron scattering and strong spin fluctuation in Na$_{0.70}$CoO$_2$, and a possible proximity to the quantum critical point was also suggested. In our previous paper, singular electronic transport and magnetic and thermodynamic properties have been observed in Mn-doped Na$_{0.70}$CoO$_2$, revealing enhanced magnetic fluctuation and possible quantum critical behavior. These results make us think about the manganese doping extreme Na$_{0.70}$MnO$_2$ compound, where all the cobalt ions are replaced by the manganese ions. It is fundamentally interesting to study the magnetotransport properties of Na$_{0.70}$MnO$_2$ and how the spin degrees of manganese ions of this compound acclimatize themselves to the geometrical frustrations. Fortunately, hexagonal Na$_{0.70}$MnO$_2$ has the analogous structure with Na$_{0.70}$CoO$_2$, offering a good opportunity to have a comparison between them. The synthesis and structure studies of Na$_{0.70}$MnO$_2$ have been fully performed, however, the detailed magnetic measurements are still lacking. In addition, recent experiments have reported the complex ground state in some kindred compounds Na$_x$MO$_2$ ($M$=Ni, Cr). So experimental investigations of the hexagonal compound Na$_{0.70}$MnO$_2$ will shed light on the understanding of the family compounds of sodium transition-metal oxides.

In this paper, detailed measurements of magnetic and thermodynamic properties in the hexagonal compound Na$_{0.70}$MnO$_2$ are performed. It is found that canonical spin-glass transition is displayed at low temperatures. The properties of this spin-glass state (including irreversibility, hysteresis effect, long-time relaxation, magnetic entropy, and order parameter) are obtained. The origin of the spin-glass behavior is carefully analyzed, and a comparison with the magnetic properties of Na$_{0.70}$CoO$_2$ is addressed.

EXPERIMENT

Polycrystalline samples with nominal composition Na$_{0.70}$MnO$_2$ were prepared by the solid-state reaction method. The detailed preparation procedure can be found in the published work of Paulsen and Dahn. The x-ray-diffraction study was performed by using a Rigaku D/max-RB in the $\theta$-2$\theta$ scan mode from 10° to 70°. Transmission electron microscopy was carried out on a JEM-200CX operating at a voltage of 200 kV. The specific heat was measured on a Quantum Design physical properties measurement system by using the thermal relaxation method. The sample, about 30 mg in weight, was thermally anchored to the sample holder, and the temperature dependence of heat capacity of the sample holder and the thermometer on it are carefully calibrated. The error of the specific-heat measurement is within 1%. The electrical resistivity was measured by using the four-probe method and gold as the electrical contact. The dc and ac susceptibilities, magnetization, and magnetic relaxation were measured by using a Quantum Design magnetic...
properties measurement system. The sample (about 50 mg in weight) was mounted in a plastic capillary, and the magnetic field was parallel to the sample surface.

RESULTS AND DISCUSSIONS

Figure 1 shows the x-ray-diffraction pattern of Na_{0.70}MnO_{2}, indicating a single phase of hexagonal structure. The lattice constants can be calculated: \( a = 2.881 \, \text{Å} \) and \( c = 11.118 \, \text{Å} \). The inset of Fig. 1 displays the electron-diffraction patterns for Na_{0.70}MnO_{2} taken along the [001] zone-axis direction. All diffraction spots can be well indexed by a hexagonal unit cell. In contrast to the sodium ordering in Na_{0.70}CoO_{2}, no diffraction spots related to Na ions vacancy superlattices have been observed. The lattice constants calculated from electron diffractions are consistent with that from x-ray diffraction within the experimental error of 2%. The electrical resistivity is characterized above 240 K, and no apparent magnetoresistance is observed at 5 T. The resistivity below 240 K is so large that it exceeds the limit of our experimental apparatus.

Figure 2(a) displays the zero-field-cooled (ZFC) and field-cooled (FC) magnetic susceptibilities of Na_{0.70}MnO_{2} measured at \( H = 25 \, \text{Oe} \). The ZFC and FC susceptibility curves start to divaricate below 50 K. The splitting of a ZFC and FC susceptibility at low temperatures could be a hallmark of a spin-glass transition. A peak of the ZFC susceptibility is exhibited at \( T_f \approx 34 \, \text{K} \). The inverse ZFC susceptibility is displayed in the inset of Fig. 2(a), including a Curie-Weiss law \( \chi = C/(T - \theta_W) \) fitting to the data above 150 K. An effective magnetic moment is determined to be \( 4.77 \, \mu_B \) per Mn ion from the Curie constant \( C \), so the Mn ions are considered to be a mixture of Mn^{3+} (\( S = 2, \mu = 4.90 \, \mu_B \)) and Mn^{4+} (\( S = 3/2, \mu = 3.87 \, \mu_B \)). The Weiss temperature is found to be \( \theta_W = -411 \, \text{K} \), indicating a single phase of hexagonal structure. The lattice constants can be calculated: \( a = 2.881 \, \text{Å} \) and \( c = 11.118 \, \text{Å} \). The inset of Fig. 1 displays the electron-diffraction pattern taken along the [001] zone-axis direction. All diffraction spots with strong intensity can be well indexed by a hexagonal unit cell. In contrast to the sodium ordering in Na_{0.70}CoO_{2}, no diffraction spots related to Na ions vacancy superlattices have been observed. The lattice constants calculated from electron diffractions are consistent with that from x-ray diffraction within the experimental error of 2%. The electrical resistivity is characterized above 240 K, and no apparent magnetoresistance is observed at 5 T. The resistivity below 240 K is so large that it exceeds the limit of our experimental apparatus.

Figure 2(b) shows the ZFC susceptibility measured at various magnetic fields. Each ZFC susceptibility curves measured at various magnetic fields. Each ZFC susceptibility curves measured at various magnetic fields. Each ZFC susceptibility curve exhibits a peak, which becomes broader and shifts to lower temperatures with increasing magnetic fields. So, higher magnetic fields suppress the energy barriers and thus reduce the freezing temperature, consistent with a spin-glass transition.

Spin-glass behavior is usually characterized by the ac susceptibility, and the freezing temperature is accurately determined by the position of the cusp of the real part of the ac susceptibility \( \chi' \). Figure 3 shows \( \chi'(T, \omega) \) measured with a driving field of 3.5 Oe. Below the freezing temperature \( T_f \approx 39 \, \text{K} \), the amplitude of \( \chi' \) highly depends on the measuring
Importantly, the peak of ac susceptibility shifts to lower temperatures with decreasing measuring frequency. Such a frequency shift is not expected for the usual antiferromagnetic or ferromagnetic long-range-ordered system. Moreover, the frequency shift defined by \( K = \frac{1}{T_f} \Delta \log \omega \) is calculated as 0.004, which is in the range of conventional spin-glass systems such as AuMn \((K=0.0045)\) and CuMn \((K=0.005)\), but much smaller than that of typical superparamagnet \( \alpha\)-Ho\(_2\)O\(_3\)(B\(_2\)O\(_3\)) \((K=0.28)\). The \( K \) value offers an experimental criterion to exclude the superparamagnetism from the Na\(_{0.70}\)MnO\(_2\) compound and favors the spin-glass behavior. In fact, the Mn ions are strongly interacting on the triangular lattice, and the concept of independent superparamagnetic particles does not apply in this compound.

To further characterize the magnetic properties of Na\(_{0.70}\)MnO\(_2\) at low temperatures, we have measured the magnetic-field dependence of magnetization \( M(H) \) (Fig. 4) and long-time magnetization relaxation \( M(t) \) (Fig. 5). The \( M(H) \) curve departs from linear relation at 50 K, and hysteresis effect is significant at lower temperatures. The coercive field \( H_c(T) \) is about several decades of oersteds from 30 to 20 K, which is comparable to that observed in conventional spin-glass systems. The increase of the coercive field at 10 K is due to the high freezing degree together with the small thermal activation energy. The zero-field-cooled magnetization relaxation is measured at different temperatures with a fixed measuring field of 200 Oe. However, the magnetization \( M(t) \) does not display any sign of saturation even after 5000 s below 30 K, indicating that the system is far from the equilibrium. It is generally believed that the long-time magnetization relaxation should be attributed to the glassy compound when the field is larger than the coercive field. Since the coercive fields at 25 and 20 K are sufficiently smaller than 200 Oe, the relaxation of \( M(t) \) should result from glassy processes. When the coercive field is comparable to the measuring field, a much larger part of the system contributes to the magnetization relaxations at 15 K. To check whether there are any general parameters describing the spin dynamics in the magnetization relaxation, we fit our data with the standard stretched exponential function

\[
M(t) = M_0 - M_r \exp \left[ -\left( \frac{t}{\tau_r} \right)^{1-n} \right],
\]

where \( M_0, M_r, \tau_r, \) and \( n \) are the ferromagnetic component, the glassy component, the relaxation characteristic time, the critical exponent, respectively. The fitting parameters are listed in Table I. The critical exponent \( n \) \((\approx 0.5)\) does not

![FIG. 3. (Color online) Temperature dependence of the real part of the ac magnetic susceptibility \( \chi' \) measured at \( \omega/2\pi=1, 10, 100, \) and 1000 Hz, respectively, with a driving field of 3.5 Oe. The inset shows the frequency dependence of the peak position plotted as \( T_f \) vs \( \omega/2\pi \).](image1)

![FIG. 4. (Color online) Magnetization as a function of the external magnetic field at \( T=80, 50, 30, \) and 10 K. The inset shows the temperature dependence of the coercive field.](image2)

![FIG. 5. (Color online) Time dependence of normalized magnetization \( M(t)/M(0) \) at different fixed temperatures. In each measurement, the sample was first cooled under zero field from 200 K, and then a field of 250 Oe was applied. The time at which the field was stable is set as the initial time \( t=0 \).](image3)
vary with temperature, and it is the interaction strength between the local magnetic moments that governs the dynamic processes. It is noted that the value of $\tau_r$ is very sensitive to the experimental conditions [as indicated by the thermoremanent magnetization (TRM) results below], so the temperature variations of $\tau_r$ cannot be concluded from the present results.

A crucial feature of the spin-glass behavior is the existence of extremely slow spin relaxation, and this dynamics process is frequently studied by the TRM measurements. The magnetization decay strongly depends on the waiting time ($t_w$) at a particular temperature before a sudden change of the magnetic field, i.e., the aging effect. In each measurement, the Na$_{0.70}$MnO$_2$ sample is cooled from the paramagnetic state with a magnetic field in Table II. We found that the relaxation characteristic time $\tau_r$ is dependent on the waiting time ($t_w$). In fact, the spin relaxation in the spin-glass state has a wide relaxation-time spectrum $g_{t_w}(\tau)$, instead of a single characteristic response time $\tau_r$. The magnetization decay can be described as

$$M_{t_w}(t) = \int_{t_0}^{\infty} g_{t_w}(\tau) \exp\left(-\frac{t}{\tau_r}\right) d\tau,$$

in which $t_0\approx 10^{-12}$ s is a microscopic attempt time. So, a relaxation function $S(t) = -\frac{1}{\mu_0 H} \frac{dM(t)}{dt \log t}$ can be used to probe the distribution function $g_{t_w}(\tau)$. The relaxation function $S(t)$ [Fig. 6(b)] exhibits a broad peak at $t\approx 250$ s for $t_w=180$ s. The peak of $S(t)$ curves shifts to larger time and becomes dispersed with increasing $t_w$. The fact that $S(t)$ does not exhibit a peak at $t=\infty$ for larger $t_w$ suggests that the dynamic process of the spin-glass state should be governed by a reduced effective waiting time $\lambda/t_w^\mu$ defined by

$$\lambda = \frac{(t + t_w)^{1-\mu} - (t_w)^{1-\mu}}{1 - \mu},$$

where $\mu$ is a fitting parameter. Figure 7 shows that the magnetization decay can be well scaled with $\lambda/t_w^\mu$ both for $H_{cooled}=10$ Oe and $H_{cooled}=2.5$ Oe. In both cases, the value $\mu<1$ is used, related to the so-called subaging effect. The scaling of the magnetization decay reveals that the spin-glass system has strong dynamic correlations among the spin degrees of freedom and cannot be regarded as a simple disorder aggregate.

![FIG. 6. (Color online) (a) Thermoremanent magnetization $M(t)$ and (b) relaxation function $S(t)$ after waiting at $T=20$ K and $H_{cooled}=10$ Oe for various times $t_w$.](image)

To describe the spin-glass state theoretically, Edwards and Anderson introduced a spin-glass order parameter $q$ as a function of temperature. Based on the appropriate form of the mean-field theory, Sherrington and Kirkpatrick predicted that the spin-glass order parameter $q(T)$ vanishes at $T_f$ as $q(T) \propto (1-T/T_f)$ below $T_f$. The value of $q(T)$ can be extracted from the dc magnetic susceptibility $\chi(T)$, the Curie constant $C_{SG}$, and the Weiss temperature $\theta_{SG}$ as follows:

$$q(T) = C_{SG}(T - \theta_{SG})$$

where $C_{SG}$ and $\theta_{SG}$ are the Curie constant and the Weiss temperature, respectively. The Weiss temperature can be obtained from the slow magnetization of $H=10$ Oe.

<table>
<thead>
<tr>
<th>$t_w$ (s)</th>
<th>$M_0$ (emu/mol)</th>
<th>$M_r$ (emu/mol)</th>
<th>$\tau_r$ (s)</th>
<th>$n$</th>
</tr>
</thead>
<tbody>
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<td>-1.60</td>
<td>712</td>
<td>0.519±0.012</td>
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<tr>
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<tr>
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<td>-1.84</td>
<td>903</td>
<td>0.511±0.012</td>
</tr>
<tr>
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<td>20.68</td>
<td>-1.85</td>
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<td>20.73</td>
<td>-1.91</td>
<td>1040</td>
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</tr>
</tbody>
</table>
the order parameter exhibits the relation $q = 1 - T_f / T_{SG}$, which is typically observed in the spin glass above the freezing temperature $T_f$. In the present compound, $Na_{0.70}MnO_2$ includes the contributions from both the lattice specific heat ($C_l$) and the magnetic specific heat ($C_m$). However, in the high-temperature paramagnetic state, $C_l$ dominates. To estimate the magnetic specific heat ($C_m$), we first determine the Debye temperature, and then subtract the lattice contribution. The Debye temperature $\theta_D$ of $Na_{0.70}MnO_2$ is determined by fitting $C_l$ above 160 K with the Debye specific-heat expression $C_l(T) = 3Nk_B\theta_D^3/(\pi^2T)^2$, in which $f_D(y) = \frac{3}{2} \int_0^{\infty} \frac{\sin x}{x^2} \, dx$ and $N = 3.7$ is the number of atoms per unit. The Debye temperature is thus obtained: $\theta_D = 578$ K. We found a broad peak in the magnetic specific heat $C_m$, which is typically observed in the spin glass above the freezing temperature $T_f$.

Below $T_f$, the magnetic specific heat behaves as $C_m = aT^{1.5}$, where $a$ is a fitting parameter. It is noted that though $C_m \propto T$ is expected as a low-temperature signature of a spin glass, a $T^{1.5}$ dependence of $C_m$ has also been observed in some of the diluted magnetic alloys regarded as canonical spin-glass systems. Moreover, in the geometrically frustrated compound $Yb_2Mn_2O_7$ with spin-glass behavior, the $T^{1.5}$ behavior of $C_m$ is attributed to spin-wave-like excitations in the intermediate range. In the present compound, $Na_{0.70}MnO_2$, the magnetic specific heat drops to zero at $T_f$, where $T_f = 38.4$ K and the lower inset of Fig. 8 displays the inverse ZFC susceptibility curves at large fields are rather broad, and the $T_f(H)$ values are simply not well defined. Other techniques including the ac susceptibility measurements with biased dc fields are under consideration for the further study of the field effect in this compound.

Figure 9 shows the results of specific-heat measurement for $Na_{0.70}MnO_2$. Generally, the measured specific heat ($C_l$) in $Na_{0.70}MnO_2$ includes the contributions from both the lattice specific heat ($C_l$) and the magnetic specific heat ($C_m$). However, in the high-temperature paramagnetic state, $C_l$ is dominating. To estimate the magnetic specific heat ($C_m$), we first determine the Debye temperature, and then subtract the lattice contribution. The Debye temperature $\theta_D$ of $Na_{0.70}MnO_2$ is determined by fitting $C_l$ above 160 K with the Debye specific-heat expression $C_l(T) = 3Nk_B\theta_D^3/(\pi^2T)^2$, in which $f_D(y) = \frac{3}{2} \int_0^{\infty} \frac{\sin x}{x^2} \, dx$ and $N = 3.7$ is the number of atoms per unit. The Debye temperature is thus obtained: $\theta_D = 578$ K. We found a broad peak in the magnetic specific heat $C_m$, which is typically observed in the spin glass above the freezing temperature $T_f$. Below $T_f$, the magnetic specific heat behaves as $C_m = aT^{1.5}$, where $a$ is a fitting parameter. It is noted that though $C_m \propto T$ is expected as a low-temperature signature of a spin glass, a $T^{1.5}$ dependence of $C_m$ has also been observed in some of the diluted magnetic alloys regarded as canonical spin-glass systems. Moreover, in the geometrically frustrated compound $Yb_2Mn_2O_7$ with spin-glass behavior, the $T^{1.5}$ behavior of $C_m$ is attributed to spin-wave-like excitations in the intermediate range. In the present compound, $Na_{0.70}MnO_2$, the magnetic specific heat drops to zero at $T_f$, where $T_f = 38.4$ K and the lower inset of Fig. 8 displays the inverse ZFC susceptibility curves at large fields are rather broad, and the $T_f(H)$ values are simply not well defined. Other techniques including the ac susceptibility measurements with biased dc fields are under consideration for the further study of the field effect in this compound.

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The Curie constant ($C_{SG} = 0.651$ emu K/mol Oe) and the Weiss temperature ($\theta_{SG} = 38.4$ K) have been obtained by fitting the susceptibility with the Curie-Weiss law from 46 to 60 K. Figure 8 displays the temperature dependence of the spin-glass order parameter $q(T)$. It can be seen that $q(T)$ drops to zero at $T_f$. In the present compound, $Na_{0.70}MnO_2$, the order parameter exhibits the relation $q(T) \propto (1 - T/T_f)^{\beta}$ (the lower inset of Fig. 8), with the critical exponent $\beta = 1.01 \pm 0.01$. This result is in good agreement with the prediction of the mean-field theory ($\beta = 1$). Based on the mean-field model of Sherrington and Kirkpatrick, de Almeida and Thouless (AT) studied the spin-glass state in finite magnetic fields and obtained a $H-T$ phase diagram of the spin-glass system. The phase boundary between stable and unstable states is called the AT line, which has the form $T_f \propto H^{1.5}$.

In the present compound, $Na_{0.70}MnO_2$, the field dependence of $T_f(H)$ [displayed in the inset of Fig. 2(b)] does not follow the AT line. However, we should mention that it is hard to define a dividing line between the stable and unstable states at finite magnetic fields. For example, the long-time relaxation can be presented even above $T_f(H)$ for a large field (such as $T = 25$ K with $H = 200$ Oe). Moreover, the peaks of ZFC susceptibility curves at large fields are rather broad, and the $T_f(H)$ values are simply not well defined. Other techniques including the ac susceptibility measurements with biased dc fields are under consideration for the further study of the field effect in this compound.

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that the hexagonal Na$_{0.70}$MnO$_2$ exhibits canonical spin-glass behavior at low temperatures. The ac susceptibility cusp at $T_f=39$ K and frequency-dependent susceptibility have been observed. The ZFC and FC susceptibility curves diverge below $T_f$, with magnetic hysteresis feature of a spin glass. The magnetic relaxation reveals that this system is metastable below $T_f$. To achieve a further understanding of Na$_{0.70}$MnO$_2$, we have to find the origin of spin-glass behavior. In the hexagonal Na$_{0.70}$MnO$_2$, the crystal structure consists of Mn-O layers and sodium ions between them. The spins of Mn ions within Mn-O plane form a triangular network, which is expected to cause magnetic frustrations. The ratio $f=\theta_W/T_f$ calculated from susceptibility measurements supports the presence of strong spin frustrations. Beyond the dominant antiferromagnetic coupling, short-range ferromagnetic order is well developed at low temperatures, indicated by the magnetic specific heat $C_m$ and the positive Weiss temperature around $T_f$ ($\theta_W=38.4$ K). The competitions of antiferromagnetic and ferromagnetic coupling are expected to cause magnetic instability, and the exact spin configurations in the ground state are very sensitive to the experimental conditions. Microscopically, the Mn$^{3+}$/4+-O-Mn$^{3+}$/4+ direct interaction is in antiferromagnetic coupling, while the Mn$^{3+}$/4+-O-Mn$^{3+}$/4+ superexchange is in ferromagnetic coupling, according to Goodenough.\textsuperscript{33} In the present compound, Na$_{0.70}$MnO$_2$, Mn ions are considered as a mixture of Mn$^{3+}$ ($S=2$) and Mn$^{4+}$ ($S=3/2$) ions. The distributions of Mn$^{3+}$/Mn$^{4+}$ are influenced by Na$^+$ ions, and no sign of electron-diffraction spots related to Na$^+$ ion ordering has been observed. So, the Mn$^{3+}$/Mn$^{4+}$ mixture is expected to distribute on the triangular lattice randomly. Based on this argument, geometrical frustration and Mn$^{3+}$/Mn$^{4+}$ mixture are likely to play a crucial role in the formation of the spin-glass state.

Finally, we compare the magnetic properties of Na$_{0.70}$MnO$_2$ with that of Na$_{0.70}$CoO$_2$. According to the previous reports, Na$_{0.70}$CoO$_2$ exhibits the Curie-Weiss form susceptibility $\chi=C/(T-\theta_W)$, with $\theta_W=-100$ K.\textsuperscript{11,12,34} Since $\theta_W$ is determined by the antiferromagnetic coupling strength of the magnetic ions, the results suggest that the antiferromagnetic coupling is stronger in Na$_{0.70}$MnO$_2$ ($\theta_W=-411$ K) than that in Na$_{0.70}$CoO$_2$. The mobility of Na$^+$ ions in Na$_{0.70}$CoO$_2$ is so large that they tend to form well ordered superstructure, which is shown by the electron diffractions\textsuperscript{7} and NMR experiments.\textsuperscript{11} In contrast to the spin-glass transition at 39 K in Na$_{0.70}$MnO$_2$, $\chi(T)$ of Na$_{0.70}$CoO$_2$ increases rapidly at low temperatures, and no magnetic transition occurs down to 1.5 K.\textsuperscript{11} It is noticeable that the susceptibility$^{12,33} \chi(T)$ and thermopower$^6$ of Na$_{0.70}$CoO$_2$ have strong field dependences due to the suppressions of spin fluctuations and spin degrees of freedom by magnetic field. Thus, geometrical frustrations induce a magnetic instability in Na$_{0.70}$CoO$_2$, and such a magnetic instability coupled with the high-mobility carriers is expected to play a key role in the formation of complex phase diagram. However, the electrical resistivity in Na$_{0.70}$MnO$_2$ is so large that the low-temperature electronic properties are hard to be detected. If the carrier density is increased to make Na$_x$MnO$_2$ become metallic, the coupling of electronic and magnetic frustrations may also emerge in this system. The related studies\textsuperscript{36} indicated that the electrical conductivity of Na$_{0.70}$MnO$_2$ can be changed remarkably by removing some sodium ions, revealing the possibility of controlling the physical properties of Na$_x$MnO$_2$ by adjusting the amount of sodium ions in the structure. Further electronic experiments on Na$_x$MnO$_2$ are needed to understand the complex ground state of triangular lattice antiferromagnets.

In conclusion, we have studied the magnetic and thermodynamic properties of the hexagonal insulating compound Na$_{0.70}$MnO$_2$. The characteristics of the canonical spin-glass transition have been observed. Irreversibility, frequency dependence of ac susceptibility, magnetic hysteresis, long-time relaxation, and cusp of the magnetic specific heat have been discussed. The spin-glass formation is ascribed to the complexity of the Mn$^{3+}$/Mn$^{4+}$ mixtures with strong geometrical frustrations.
ACKNOWLEDGMENTS

We thank C. M. Xiong for helpful discussions. This work was supported by the National Science Foundation of China (Grants No. 50425205, No. 10674079, and No. 50272031), the 973 project (No. 2002CB613505), Specialized Research for the Doctoral Program of Higher Education (No. 20030003088), and National Center for Nanoscience and Technology of China.

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