Spontaneous magnetization and resistivity steps in the bilayered manganite 
\( (La_{0.5}Nd_{0.5})_{1.2}Sr_{1.8}Mn_2O_7 \)

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We report a detailed study of steplike magnetization and resistivity jumps in a bilayered 
\( (La_{0.5}Nd_{0.5})_{1.2}Sr_{1.8}Mn_2O_7 \) single crystal. The sample exhibits very sharp metamagnetic transitions at low temperature when the magnetic field is applied either in an \( ab \) plane or along the \( c \) axis, which causes huge magnetization steps. The critical field depends on the cooling magnetic field as well as the sweep rate of the magnetic field. Meanwhile, the evolution with time of the magnetization exhibits a spontaneous step when both the temperature and magnetic field are constant. Similar steplike behaviors are also observed in resistivity. These results suggest that a martensiticlike transformation could happen in bilayered manganites.

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I. INTRODUCTION

Recent research on perovskite manganites has revealed that the physical properties of these compounds are governed by the coexistence and competition of different magnetic and electronic phases, such as the ferromagnetic (FM) metallic phase, charge/orbital ordered (CO/OO) insulating phase, and paramagnetic insulating phase, etc. In a phase-separated ground state, external disturbance, such as magnetic field, may drive the transformation among different phases. A good example is the magnetic-field-induced metamagnetic phase transition from a paramagnetic or antiferromagnetic (AFM) phase to a FM phase. Metamagnetic transitions in manganites have been studied primarily at temperatures above 5 K, and the transitions are rather broad in that temperature regime. However, at temperatures below 5 K, the metamagnetic transitions may become very sharp, i.e., occur by “magnetization steps,” as observed in some \( R_{1-x}A_xMnO_3 \) manganites, such as \( Pr_{0.6}Ca_{0.4}MnO_3 \) (Ref. 3), \( Pr_{0.5}Ca_{0.5}MnO_3 \) (Ref. 4), \( Pr_{0.5}Ba_{0.5}MnO_3 \) (Ref. 5), and \( Pr_{0.5}Sr_{0.5}MnO_3 \) (Ref. 6). These magnetization steps were found to be sensitive to the magnetic field sweep rate as well as the cooling magnetic field. Moreover, Hardy et al. recently observed spontaneous magnetization jumps in the time evolution of magnetization in \( Pr_{0.5}Ca_{0.5}MnO_3 \) (Ref. 6) when both the magnetic field and temperature are constant. The origin of these phenomena is still a matter of controversy. Different interpretations have been proposed. Most of the authors think that a martensiticlike transformation is the origin of the magnetization jumps. The interpretation of a martensiticlike transformation in \( R_{1-x}A_xMnO_3 \) manganites is based on the scenario of phase separation in which the (CO/OO) AFM regions coexist and compete with FM regions. The slightly different cell parameters of the FM and (CO/OO) AFM phase generate strains at the interface regions, similar to the strain accommodation observed in martensitic phase transitions, which impedes the structural transition. At low temperature in the majority (CO/OO) AFM phase, the growth of the FM regions around the FM nucleation centers is favored by the applied magnetic field. As the field is large enough for the driving force acting on the spins to overcome the elastic constraints, the local stress field is destabilized in a burstlike process, which causes a sudden jump in magnetization.

Apart from cubic \( R_{1-x}A_xMnO_3 \) manganites, magnetization steps have also been reported in certain bilayered manganites such as \( (La_{0.4}Pr_{0.6})_{1.2}Sr_{1.8}Mn_2O_7 \). Magnetostriiction and lattice relaxation measurements indicate that the magnetization step involves significant lattice changes. However, compared with \( R_{1-x}A_xMnO_3 \) manganites, the behavior of magnetization steps in bilayered manganites has not been studied in detail and its origin has not been clarified. In this paper, we present a detailed study of the magnetization in a bilayered \( (La_{0.5}Nd_{0.5})_{1.2}Sr_{1.8}Mn_2O_7 \) single crystal at low temperature. Magnetization steps are observed at 2 K when the field is applied either in the \( ab \) plane or along the \( c \) axis. The critical field at which the magnetization step occurs increases linearly with cooling field. Moreover, a spontaneous step of magnetization is observed in relaxation experiments when both the temperature and magnetic field are constant. In addition, the steplike behaviors are also observed in resistivity. These results, similar to those observed in some half-doped \( R_{1-x}A_xMnO_3 \) manganites, are discussed in terms of a martensiticlike transformation associated with phase separation in bilayered manganites.

II. EXPERIMENTS

A single crystal of \( (La_{0.5}Nd_{0.5})_{1.2}Sr_{1.8}Mn_2O_7 \) was 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 crystal. X-ray diffraction (XRD) and back-reflection Laue XRD experiments were taken to check the crystallization and determine the crystallographic direction. Powder x-ray diffraction measurements at room temperature and Rietveld analysis indicate that the crystal is single phase and has a tetragonal \( (I4/mmm;Z=2) \) symmetry. A rectangular piece of \( (La_{0.5}Nd_{0.5})_{1.2}Sr_{1.8}Mn_2O_7 \) single crystal was cut off to take the magnetization and resistivity measurements. The magnetic and resistive measurements were
performed by using in a commercial physical properties measurement system (Quantum Design PPMS-14).

III. RESULTS AND DISCUSSION

Figure 1 presents the magnetization of \((\text{La}_{0.5}\text{Nd}_{0.5})_{1.2}\text{Sr}_{1.8}\text{Mn}_2\text{O}_7\) as a function of temperature in a 1000 Oe magnetic field with \(H//ab\) plane and \(c\) axis, respectively. The magnetization was measured with both the zero-field-cooled (ZFC) and field-cooled (FC) processes. For both directions, there is a big divergence between ZFC and FC magnetization below a freezing temperature \(T_f\), which suggests that there is no long-range magnetic ordering at low temperature. The freezing temperature \(T_f\) is about 35 K for \(H//ab\) plane and 30 K for \(H//c\) axis. Meanwhile, the higher magnetization along the \(c\) axis suggests that the easy magnetizing direction is along the \(c\) axis, which is in contrast to the case in the \(\text{La}_{1.3}\text{Sr}_{1.8}\text{Mn}_2\text{O}_7\) system where the direction of easy magnetization is in the \(ab\) plane.\(^{12}\) This is due to the lattice changes induced by Nd doping. In \(\text{La}_{1.3}\text{Sr}_{1.8}\text{Mn}_2\text{O}_7\), the \(e_g\) electrons occupy the planar \(d_{z^2-r^2}\) orbit of \(\text{Mn}^{3+}\), which are responsible for the long-range ferromagnetic ordering. However, Nd substitution on the La site causes an elongation of \(c\) axis and a shrinkage of \(a\) axis, which leads to a change in the \(e_g\)-electron occupation from the \(d_{z^2-r^2}\) to the \(d_{x^2-y^2}\) orbit which is perpendicular to the \(\text{MnO}_2\) planes. Though Nd doping does not affect the Mn-O-Mn bond angle in the \(ab\) plane, it weakens the FM interaction because the transfer integral of \(d_{z^2-r^2}\) state is smaller than that of \(d_{x^2-y^2}\) state.\(^{13,14}\) A previous study in \(\text{La}_{1.2}\text{Sr}_{1.8}\text{Mn}_2\text{O}_7\) has shown that there exists short-range charge and orbital ordering in the paramagnetic phase, but disappears below \(T_c\).\(^{15}\) In \((\text{La}_{0.5}\text{Nd}_{0.5})_{1.2}\text{Sr}_{1.8}\text{Mn}_2\text{O}_7\) 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. There have been plenty of experiments to indicate phase separation in bilayered manganites.\(^{1,2}\) Especially, nuclear magnetic resonance and Hall effect measurements suggest a tendency of phase separation at low temperature in \(\text{La}_{1.2}\text{Sr}_{1.8}\text{Mn}_2\text{O}_7\).\(^{16,17}\) Thus, it is proposed that \((\text{La}_{0.5}\text{Nd}_{0.5})_{1.2}\text{Sr}_{1.8}\text{Mn}_2\text{O}_7\) is in a phase-separated state at low temperature in which nanoscale FM clusters coexist with the short-range charge/orbital ordered regions. In fact, a similar phase-separation picture has been proposed for \((\text{La}_{0.8}\text{Pr}_{0.2})_{1.2}\text{Sr}_{1.8}\text{Mn}_2\text{O}_7\).\(^{18}\)

Figure 2(a) shows the \(M-H\) curves of the \((\text{La}_{0.5}\text{Nd}_{0.5})_{1.2}\text{Sr}_{1.8}\text{Mn}_2\text{O}_7\) single crystal at 5 and 2 K with \(H//c\) axis after a ZFC process. In these measurements, the magnetic field is swept at a rate of 40 Oe/s. At 5 K, the \(M-H\) curve begins with a slow increase in low magnetic fields. Then, a rapid increase of magnetization starts at \(H\approx 5\ T\), evidencing a metamagnetic transition. Above 8 T, the magnetization smoothly tends to saturation. The field-induced transformation is irreversible, as clearly demonstrated by the descending branch of the \(M-H\) curve which is almost flat down to \(\sim 1\ T\) and then follows a rapid decrease as \(H\) tends to zero. The width of the field-induced metamagnetic phase transitions at 5 K is very broad, approximately 3 T (from 5 to 8 T), which indicates a wide distribution of critical fields which drive this transition in different parts of the sample. This is consistent with the presumption of phase separation in \((\text{La}_{0.5}\text{Nd}_{0.5})_{1.2}\text{Sr}_{1.8}\text{Mn}_2\text{O}_7\).

In contrast, the \(M-H\) curve at 2 K exhibits more peculiar behavior. The metamagnetic transition occurs at a higher field and becomes very sharp, which causes a big magnetization step. The step is followed by a smooth tail to saturation at high fields. The critical field \(H_c\) where the step occurs is 6.216 T and the transition width is less than...
500 Oe. This steplike feature in magnetization is similar to that observed in Pr$_{0.5}$Ca$_{0.5}$Mn$_{0.95}$Co$_{0.05}$O$_3$ at $T=3$ K. The relative magnitude of the step can be written as $g = \Delta M / M_{sat} = 46.09\%$ at 2 K for (La$_{0.5}$Nd$_{0.5}$)$_{1.2}$Sr$_{1.8}$Mn$_2$O$_7$.

The measurements in Fig. 2 were performed with a field interval of 500 Oe, and the result shows that the width of the magnetization step at 2 K is less than 500 Oe. In order to determine the limit of sharpness of the metamagnetic transition, we also measured the $M$-$H$ curve with a field interval of 10 Oe in the vicinity of the step transition. As shown in the inset of Fig. 2(a), the critical field is 6.218 T and the step width is less than 20 Oe. The sharpness of the steps indicates that there exists a jerky growth of the ferromagnetic fraction in a phase-separation state during martensiticlike transformation.

Similarly, Fig. 2(b) shows the ZFC $M$-$H$ curves at 5 and 2 K with $H \parallel ab$ plane. A magnetization step is also observed in the $ab$ plane and the critical field is 6.714 T. The critical field is higher than that of $H \parallel c$ axis. The higher moment at lower field and the lower critical field along the $c$ axis further indicates that the easy magnetizing direction is along the $c$ axis.

It is well known that field cooling changes the relative fraction of ferromagnetic and short-range charge/orbital ordered phase, so we have also studied the effect of the cooling field on the magnetization step at $T=2$ K with $H \parallel c$ axis. For these measurements, the sample was cooled from 300 to 2 K in the respective magnetic fields. After the measurement temperature (2 K) is stable, the field is reduced to zero, then the $M$-$H$ curve is measured up to 13 T, and the results are shown in Fig. 3. When the cooling field is below 2 T, there is no obvious change in the $M$-$H$ curves before the onset of the step transition ($H < H_c$). For the 2 T field cooling, the low-field magnetization presents a slight increase. However, for the 3 T field cooling, the magnetization shows an abrupt increase at quite low field ($H < 0.4$ T), and is follow by a plateau with a smooth tail until the onset of the step transition at 6.966 T. This behavior is similar to that seen in Pr$_{0.5}$Ca$_{0.5}$Mn$_{0.95}$Co$_{0.05}$O$_3$. Field cooling apparently increases the ferromagnetic fraction in the sample at the expense of the short-range (CO/OO) phase volume at low fields and thus results in a larger low-field magnetization, which is very obvious for the 3 T field cooling. Although field cooling increases the low-field magnetization at temperatures below the onset of the step transition, the critical field ($H_c$) increases after field cooling, which is a surprising phenomenon since field cooling should enhance ferromagnetic fraction. Meanwhile, the shift of $H_c$ is almost linear with the increase of cooling field, as shown in the inset of Fig. 3. Such a shift of the magnetization step with the cooling field was also observed in Pr$_{0.5}$Ca$_{0.5}$Mn$_{0.95}$Co$_{0.05}$O$_3$. We think that field cooling changes strains at the interface regions, making them more difficult to transform into a highly polarized state in martensiticlike phase transitions.

One important feature supporting a martensitic scenario rather than a standard metamagnetism in manganites is the influence of the average magnetic field sweep rate. Therefore, we checked the sweep rate dependence of magnetization steps for $H \parallel c$ axis. As shown in Fig. 4, the magnetization step strongly depends on the sweep rate of field. With increasing sweep rate, the critical field decreases, from 6.704 T for 10 Oe/s to 5.738 T for 100 Oe/s. It was proposed that a smaller sweep rate can facilitate the progressive accommodation of the martensitic strains and delay the magnetic instability, pushing the steps to higher field values. In order to investigate more directly the dynamics of the magnetization jumps, we also carried out relaxation experiments on the sample with $H \parallel c$ axis. Since the $H_c$ of ZFC curve at 2 K is 6.216 T, we studied the relaxation with applied fields slightly below and above $H_c$. The relaxation experiments were measured by the following sequence: (i) the sample was first zero-field cooled from room temperature down to 2 K; (ii) after the temperature is stable, a field of 6.2 T was applied and the magnetization was recorded as a function of time. This procedure was repeated in a range of magnetic fields around 6.2 T and the result is shown in Fig. 5. For $H=6.2$ T, there exists a spectacular magnetization jump when measuring as a function of time and similar
result is observed in Pr$_0.5$Ca$_0.5$Mn$_{0.97}$Ga$_{0.03}$O$_3$ and Pr$_0.5$Ca$_0.5$Mn$_{0.95}$Ga$_{0.05}$O$_3$. The interesting phenomenon is the fact that this class of bilayered manganites can display a spontaneous jump in magnetization when both the temperature and magnetic field are constant. We have checked the quality of the temperature stabilization over the duration of the relaxation experiments (2,000±0.003 K). It is noticed that the magnetic field is applied by a superconducting coil in the persistent mode and is very stable during the measuring time.

The inset of Fig. 5 shows an enlargement of the relaxation curve obtained in 6.2 T for a (La$_{0.5}$Nd$_{0.5}$)$_{1.2}$Sr$_1$Mn$_2$O$_7$ single crystal. There is a slow relaxation process preceding the magnetization jump (τ<420 s). The existence of a silent time before the start of the magnetization jump is known as the “incubation time” effect, which is encountered in standard martensitic transformations. Then the relaxation curve is followed by the magnetization jump which takes place over a time interval smaller than the separation between two consecutive points, i.e., <30 s. In addition, the relaxation phenomenon is not observed after the magnetization jump. We think that the behavior at 6.2 T is an explosive instability, where the response of the magnetization presents an abrupt increase at a very short time. When both the temperature and the field are constant, the steplike magnetic relaxation reported here presents an unusual phenomenon of magnetization jump observed in bilayered manganites. In particular, the occurrence of such a jump in a constant field shows that this phenomenon is not solely driven by a change in the magnetic energy. We note that such a spontaneous magnetization jump is qualitatively consistent with the previously proposed “martensitic” scenario in which the magnetization step is proposed to correspond to a burstlike growth of the ferromagnetic fraction at the expense of the antiferromagnetic component, driven by the evolution of the strains at the interfaces between the two kinds of domains.

Figure 6 shows the same set of data as in Fig. 5 but is plotted as $M/M(0)$ versus time, where $M(0)$ is the first measurement recorded at $t=0$ for each field. We can see that the magnetic relaxation in 6.3 T actually yields a flat curve without detectable time dependence. In contrast, the curve in 6.1 T field exhibits obvious relaxation behavior. When $H$ =6.1 T, the curve can be fitted by a simple relaxation law of the form $M(t)=M_0+(M_\infty-M_0)[1-\exp(-t/\tau^\beta)]$, Where $M_0$ is the initial magnetization at $t=0$, $M_\infty$ is the magnetization at $t=\infty$, $\tau$ is the relaxation time which is related to the magnitude of the energy barrier between two metastable states, and $\beta$ is a dispersion parameter between 0 and 1 associated with the strength of interactions. This function is very similar to the Kohlrausch form, which is often used to describe the relaxation in strongly interacting materials. The fit of the relaxation curve is presented as a red solid line in Fig. 6 and the obtained fitting parameters are as follows. $M_0$ =32.688 emu/g; $M_\infty$=34.787 emu/g; $\tau$ =2507.166 s; $\beta$ =0.5963. The value of $M_\infty$/$M_{sat}$, indicating the volume fraction of the FM region in the phase-separated state, is 49.5%.

The magnetization relaxation in 6.3 T is presented as a red solid line in the inset of Fig. 7 and the obtained fitting parameters are as follows: $M_0$ =25.601 emu/g; $M_\infty$=27.222 emu/g; $\tau$ =2479.439 s; $\beta$=0.6086. Meanwhile $M_\infty$ (27.222 emu/g) in 6.6 T is below 27.753 emu/g—the critical value at which the magnetization jump occurs, which indicates that the relaxation curve in 6.6 T should also not exhibit a spontaneous jump even for extended measuring time. For comparison, we also measured the magnetization relaxation in the ab plane at 2 K and the result is presented in Fig. 7. A spontaneous magnetic jump also occurs. The “incubation time” is 510 s in $H$=6.7 T. The fit of the relaxation curve using the function $M(t)=M_0+(M_\infty-M_0)\times[1-\exp(-t/\tau^\beta)]$ in $H$=6.6 T is presented as a red solid line in the inset of Fig. 7 and the obtained fitting parameters are as follows: $M_0$ =25.601 emu/g; $M_\infty$=27.222 emu/g; $\tau$ =2479.439 s; $\beta$=0.6086. Meanwhile $M_\infty$ (27.222 emu/g) in 6.6 T is below 27.753 emu/g—the critical value at which the magnetization jump occurs, which indicates that the relaxation curve in 6.6 T should also not exhibit a spontaneous jump even for an extended measuring time.
Since there is a strong correlation between magnetic and transport properties in manganites, it would be expected that similar step-like changes could also happen in resistivity. Because the resistivity of the c axis is too large to be measured when temperature is below 37 K, we only checked the resistivity in ab plane. Figure 8 shows the ZFC R-H curves at 2 K with H // ab plane. A sudden jump of resistivity is observed at a critical field of 6.71 T which corresponds to transition field in the magnetization step. The relaxation experiments of resistivity were measured using a similar sequence of magnetic relaxation measurements. As shown in Fig. 9, a spontaneous resistive jump at 2 K in H=6.7 T is observed. Similar to the case in magnetization, there is a slow relaxation process preceding the resistivity jump (t<510 s) in H =6.7 T. The resistive relaxation in 6.8 T actually yields a flat curve without detectable time dependence. In contrast, the curve in a 6.6 T field exhibits obvious relaxation behavior and the fit of the curve is presented as a red solid line in Fig. 9 by using the function \[ -\log_{10}(\rho(t)) = 1 - \exp\left(-\left(\frac{\tau}{\rho}\right)^{\beta}\right) \]

where \( \rho(0) \) is the initial resistivity at \( t=0 \), \( \rho(\infty) \) is the resistivity at \( t=\infty \), \( \tau \) is the relaxation time, and \( \beta \) is a dispersion parameter. The obtained fitting parameters are as follows: \( \rho(0)=630.376 \ \Omega \ \text{cm}; \rho(\infty)=267.732 \ \Omega \ \text{cm}; \tau=3199.43 \ \text{s}; \beta=0.689. \)

The above behaviors of the magnetization step in the bilayered \((\text{La}_{0.5}\text{Nd}_{0.5})_{1+2}\text{Sr}_{1}\text{Mn}_{2}\text{O}_{7}\) are similar to those observed in the cubic manganites such as \(\text{Pr}_{0.5}\text{Ca}_{0.5}\text{Mn}_{0.97}\text{Ga}_{0.03}\text{O}_{3}\) and \(\text{Pr}_{0.5}\text{Ca}_{0.5}\text{Mn}_{0.95}\text{Co}_{0.05}\text{O}_{3}\) where they are attributed to a martensitic-like transformation associated with interface strain between the phase-separated regions. Therefore, we believe that a similar mechanism should also apply in bilayered manganites. The key point is that this transformation is associated with phase-separation in which FM and short-range AFM regions coexist and compete. A martensitic transformation involves a shear-induced lattice distortion between a high-\(T\) phase (austenite) and a low-\(T\) phase (martensite). Because of a significant change in shape of the unit cell, the nucleation of first martensitic domains upon cooling induces long-range, anisotropic strains developing from the martensite/austenite interfaces. The slightly different cell parameters of the FM and (CO/OO) AFM phase are obtained from X-ray diffraction measurements. Applied magnetic field drives the growth of the FM regions. As the field is large enough to drive the spins to overcome the elastic constraints, the local stress field is destabilized in a burstlike process, which causes a sudden jump in magnetization. The FM regions can spread out until a balance between the decreasing magnetic energy and increasing elastic energy may be found, leading to a magnetization plateau. In a canonical martensitic transformation, the austenite phase transforms into the martensite upon lowering temperature or applying external stress. In phase-separated manganites, the roles of austenite and martensite are played by the short-range charge/orbital order phase and ferromagnetic phases, respectively, while the increasing magnetic
field just acts as lowering temperature or increasing stress. Thus, the observed magnetization and resistivity jumps would be closely linked to this martensiticlike transformation.

IV. SUMMARY

We have demonstrated peculiar steplike magnetization and resistivity jumps at low temperature in a bilayered \((\text{La}_{0.5}\text{Nd}_{0.5})_{1.2}\text{Sr}_1\text{Mn}_2\text{O}_7\) single crystal. The width of the step is very sharp (<20 Oe). The critical field depends on the cooling magnetic field and the sweep rate of the field. Moreover, in a magnetic field slightly below the critical field, the magnetic and resistive relaxation exhibits a spontaneous step after a long incubation time when both the temperature and magnetic field are constant. These phenomena are discussed in terms of a martensiticlike transformation associated with phase separation.

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