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Dependence of giant magnetoresistance on oxygen stoichiometry and magnetization in polycrystalline $La_{0.67}Ba_{0.33}MnO_z$

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We have studied resistivity, magnetization, and magnetoresistance in polycrystalline $La_{0.67}Ba_{0.33}MnO_z$ by reducing the oxygen stoichiometry from $z=2.99$ to 2.80. As the oxygen content decreases, the resistivity of $La_{0.67}Ba_{0.33}$ MnO_z increases and the magnetic transition temperature shifts to lower temperature. A large magnetoresistance effect was observed over a wide temperature range for all samples except the insulating $z=2.80$ sample. The similarity between our results on oxygen-deficient polycrystalline $La_{0.67}$ $Ba_{0.33}MnO_z$ and films previously reported to have a very large intrinsic magnetoresistance is discussed. At low temperature the magnetoresistance was observed to be strongly dependent on the magnetization. A possible mechanism for this effect is discussed.

The phenomenon of intrinsic giant magnetoresistance (GMR) in oxides has been known for a long time.[1–3] However, recent observations of a large GMR effect in ferromagnetic metallic oxides $R_{1-x}B_xMnO_z$ (R=La,Pr,Nd, B=Ca,Sr,Ba,Pb)[4–11] have triggered renewed attention to this class of materials. An extremely large GMR effect in films of $Nd_{0.7}Sr_{0.3}MnO_z$ (Ref. 8) and $La_{0.67}Ca_{0.33}MnO_z$ (Refs. 6 and 9) have recently been reported. The magnetoresistance (MR) ratio in these films exceeds 0.999, with the MR ratio here defined as $[R(0)-R(H)]/R(H=0)$, where $R(0)$ is the resistance in zero field and $R(H)$ is the resistance in a field. The transport and magnetic properties of these films strongly depend on film preparation details, such as substrate temperature[12] and post heat treatments.[5–11]

It is believed that the double exchange interaction between pairs of Mn^{3+} and Mn^{4+} ions is responsible for the ferromagnetic and metallic properties in these manganese oxides.[13] Pairs of Mn^{3+} and Mn^{4+} can be controlled by changing the doping level or oxygen stoichiometry. Therefore, it seems plausible that oxygen content will be important for the magnetic and electronic properties in these materials. Until now the dependence of magnetic and transport properties on oxygen stoichiometry has not been investigated. In this letter we will show that the resistivity, magnetization, and magnetoresistance in bulk ceramic samples depend on oxygen stoichiometry. We will discuss a similarity between our experimental results and the prior results on films where a very large intrinsic magnetoresistance effect was observed. On the other hand, a very large magnetoresistance effect occurs not only near the ferromagnetic transition temperature (T_c),[7,10,14] but also at temperatures[9,15,16] well below T_c. We will also report the dependence of this large magnetoresistance on magnetization and present a possible explanation for the low-temperature magnetoresistive effect.

We synthesized polycrystalline $La_{0.67}Ba_{0.33}MnO_{2.99}$ by mixing La_2O_3, $BaCO_3$, and $MnCO_3$ with repeated grinding and refiring as indicated in Ref. 17. At the final stage the powders were pelletized and annealed at 1500 °C in air for 8 h. The x-ray diffraction pattern indicated that the parent $La_{0.67}Ba_{0.33}MnO_{2.99}$ material has the cubic perovskite structure without any other secondary or impurity phase. The lattice parameter is $a=3.897(\pm 0.003)$ Å. The lattice parameter of the oxygen-deficient $La_{0.67}Ba_{0.33}MnO_z$ becomes larger than that of the nearly stoichiometric sample ($z=2.99$). For example, $La_{0.67}Ba_{0.33}MnO_{2.90}$ has a lattice parameter of $3.910(\pm 0.003)$ Å. The oxygen stoichiometry was measured by iodometric titration.[18]

We annealed $La_{0.67}Ba_{0.33}MnO_{2.99}$ under many different conditions similar to those used previously for the films of $La_{1-x}Sr_xMnO_z$,[7] $La_{0.67}Ca_{0.33}MnO_z$,[6,9] $La_{0.67}Ba_{0.33}MnO_z$,[5,12] and $Nd_{0.7}Sr_{0.3}MnO_z$.[8] It was not possible to change the oxygen stoichiometry of $La_{0.67}Ba_{0.33}$ $MnO_{2.99}$ under these conditions or even under high pressure (300 bars) and high temperature (900 °C) in an O_2 atmosphere. However, by annealing with a Ti getter at 800–900 °C in a N_2 atmosphere, we have successfully reduced the oxygen content of the samples.

Magnetic measurements were carried out with a superconducting quantum interference device magnetometer in a field of up to 5 T. Resistivity was measured by the usual four point method with a typical sample size of $5\times 1\times 0.1$ mm^3. The same samples were used in both the magnetic measurement and the resistivity measurement. In the magnetic measurement the field was applied in the longest sample direction to minimize demagnetization effects, and in the resistivity measurement the field direction was perpendicular to the current direction.

The temperature dependence of the magnetization for $La_{0.67}Ba_{0.33}MnO_z$ was measured in a field of 5000 G, which is above the magnetization saturation field (H_s) (3000–4000 G) (Fig. 1). The magnitude of magnetization for oxygen content, 2.99, 2.95, and 2.90, is essentially the same at 5 K (80–87 emu/g), but the ferromagnetic transition temperature, defined as the temperature of the maximum slope in dM/dT,[19] shifts to lower temperature with the increase of oxygen deficiency. There is a significant difference in the magnitude of magnetization between oxygen content of 2.90 and 2.85. For $La_{0.67}Ba_{0.33}MnO_{2.88}$, the magnitude of magnetization becomes much smaller and the ferromagnetic transition is much broader compared with those of higher oxygen

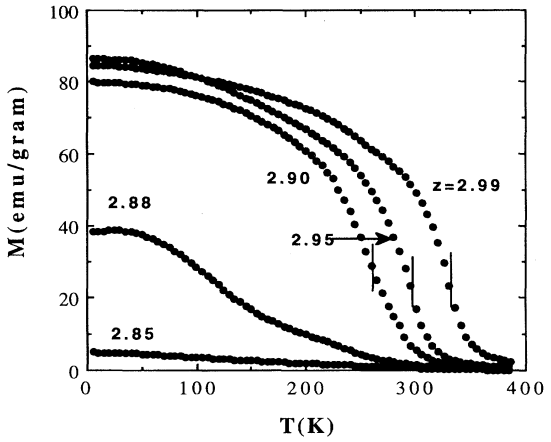

FIG. 1. Temperature dependence of magnetization for $La_{0.67}Ba_{0.33}MnO_z$ ($2.80 \leq z \leq 2.99$). The applied field was 5000 G. For $z=2.99$, 2.95, and 2.90 samples ferromagnetic transition temperature, defined as the temperature of the maximum slope in dM/dT, is indicated by a vertical line on the magnetization curve.

content samples. For $z=2.85$ the average manganese oxidation state is 3.03 and only a few pairs of Mn^{3+} and Mn^{4+} exist. Since the pairs are responsible for the ferromagnetism, this small number of pairs is consistent with the small ferromagnetic moment we measured for this composition.

The temperature dependence of the resistivity for $La_{0.67}Ba_{0.33}MnO_z$ is shown in Fig. 2. The metallic resistivity increases with decreasing oxygen content and the material becomes insulating for $z=2.80$. All samples except $La_{0.67}Ba_{0.33}MnO_{2.80}$ exhibit a resistivity peak which decreases in temperature with the increase of oxygen deficiency. Samples with oxygen stoichiometry between 2.90 and 2.85 show a rapid increase of resistivity which appears to correlate with the magnitude of magnetization which decreases rapidly for this range of oxygen content.

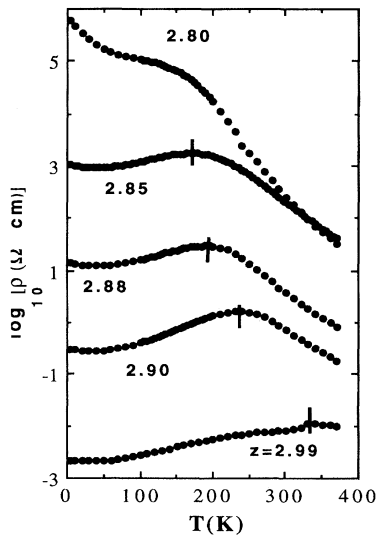

FIG. 2. Temperature dependence of resistivity for $La_{0.67}Ba_{0.33}MnO_z$ ($2.80 \leq z \leq 2.99$). A vertical line indicates the position of resistivity peaks.

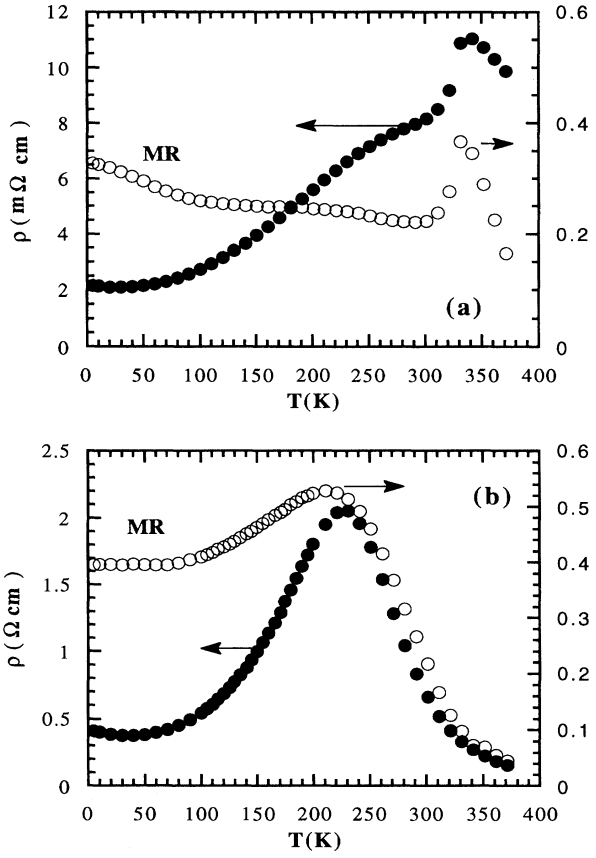

FIG. 3. Temperature dependence of resistivity (filled circle) and MR ratio (empty circle) for (a) $La_{0.67}Ba_{0.33}MnO_{2.99}$ and (b) $La_{0.67}Ba_{0.33}MnO_{2.90}$. The MR ratio is defined as $[R(0)-R(H=5T)]/R(0)$.

All the samples except $La_{0.67}Ba_{0.33}MnO_{2.80}$ show a large magnetoresistance. Figure 3 shows the temperature dependence of the resistivity and the MR ratio with an applied field of 5 T for $La_{0.67}Ba_{0.33}MnO_{2.99}$ and $La_{0.67}Ba_{0.33}MnO_{2.90}$. As seen in Fig. 3(a), for $La_{0.67}Ba_{0.33}MnO_{2.99}$, the resistivity peak was observed around 340 K. By applying a magnetic field the resistivity drops significantly throughout whole temperature range we have investigated. The MR ratio at a field of 5 T has a sharp peak at 330 K, slightly below the resistivity peak. There also exists a significant magnetoresistance below the resistivity peak which increases slightly as temperature decreases. Figure 3(b) shows the temperature dependence of the resistivity for $La_{0.67}Ba_{0.33}MnO_{2.90}$. In this case the resistivity peak is observed near 230 K, and the MR peak near 210 K. Figure 4 shows the field dependence of $R(H)/R(0)$ and the magnetization at 5 K for $La_{0.67}Ba_{0.33}MnO_{2.99}$ and $La_{0.67}Ba_{0.33}MnO_{2.90}$. This result suggests a correlation between the magnetization and the resistivity of the sample. Below the magnetic saturation field (3000–4000 G), the resistance drops rapidly with an increase of the field. Above the saturation field, the resistance drops more slowly compared to the low-field drop, but still significantly. We also find that above the saturation field, the field dependence of the resistance for $La_{0.67}Ba_{0.33}MnO_{2.90}$ is much greater than that of $La_{0.67}Ba_{0.33}MnO_{2.99}$.

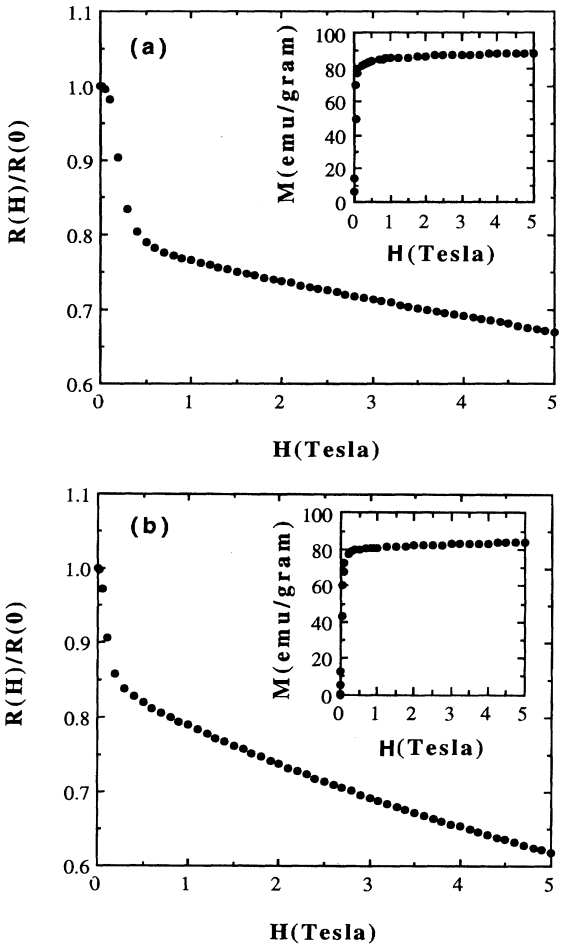

FIG. 4. Field dependence of relative resistivity and magnetization at 5 K for (a) $La_{0.67}Ba_{0.33}MnO_{2.99}$ and (b) $La_{0.67}Ba_{0.33}MnO_{2.90}$.

Now we discuss our results and compare them with prior work on films. The magnetization, resistivity, and MR behavior found in our polycrystalline $La_{0.67}Ba_{0.33}MnO_z$ are similar to those found in films of $La_{1-x}Sr_xMnO_z$,[7] $La_{0.67}Ba_{0.33}MnO_z$,[5,12] $La_{0.67}Ca_{0.33}MnO_z$,[6,9] and $Nd_{0.7}Sr_{0.3}MnO_z$.[8] In films of $La_{0.67}Ba_{0.33}MnO_z$,[12] a higher substrate growth temperature results in a higher resistivity and a lower temperature for the resistivity peak. Similarly, for polycrystalline $La_{0.67}Ba_{0.33}MnO_z$, as the oxygen content decreases, the resistivity increases and the resistivity peak temperature shifts to lower temperature. This suggests that oxygen deficiency is the origin of the resistivity behavior. Similar behavior is observed in films of $LaMnO_3$ with Sr and Ca doping.[6,7]

The lattice parameter ($a=3.89$ Å) of highly resistive $La_{0.67}Ca_{0.33}MnO_z$ films[6] is larger than that of bulk ($a=3.87$ Å) samples.[17] Similarly oxygen-deficient $La_{0.67}Ba_{0.33}MnO_z$ has a larger lattice parameter than that of stoichiometric samples [for example, $z=2.99$ and 2.90 samples have a lattice parameter $a=3.897(\pm 0.003)$ Å, $3.910(\pm 0.003)$ Å, respectively]. With increasing oxygen deficiency, the average manganese oxidation state decreases

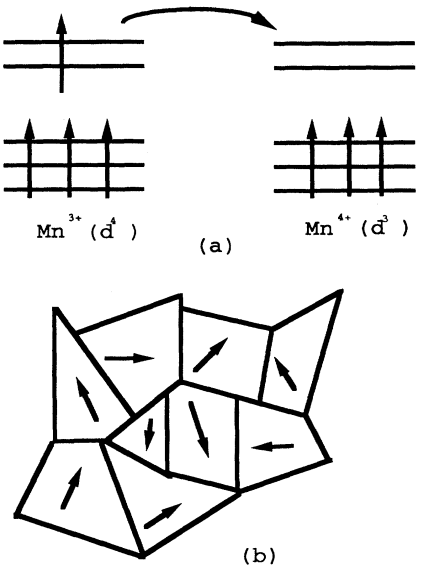

FIG. 5. (a) The double exchange mechanism which gives ferromagnetic coupling between ions participating in electron transfer between pairs of Mn^{3+} and Mn^{4+} ions. The ferromagnetic alignment of neighboring ions is required to maintain the high spin arrangement of electrons for both the donating and the receiving ions. (b) Schematic diagram for an unmagnetized specimen whose macroscopic magnetization is zero. The arrow indicates the direction of magnetization for a given domain.

and thus the average manganese ionic size increases. As a result the lattice parameter of manganese oxide may increase.

The magnetization for highly resistive films of $La_{0.67}Ca_{0.33}MnO_z$ (Ref. 6) is very similar to that for highly oxygen-deficient and resistive $La_{0.67}Ba_{0.33}MnO_{2.88}$, i.e., for both materials the magnitude of magnetization is small (~ 40 emu/g at 5 K) and the temperature dependence of the magnetization is different from that of higher oxygen content $La_{0.67}Ba_{0.33}MnO_z$ samples. Our experimental results and previous work[20,21] show that it is difficult to increase the oxygen content beyond 3 in highly doped (i.e., more than 30% doping) $LaMnO_3$. The difficulty in obtaining an excess oxygen state in these oxides is probably true for films as well. In conclusion the comparison of our experimental results with that of films strongly suggests that the films have oxygen deficiencies. By decreasing the oxygen content in our bulk samples it was possible to reproduce the MR, magnetization, and resistivity behavior observed in films of these materials.[22]

Bulk $La_{0.67}Ba_{0.33}MnO_z$ shows a magnetoresistive effect in two distinct regions. One is dominant at high temperature near the ferromagnetic temperature, the other is dominant at low temperature where the magnetization is substantial. The physical origin of the MR effect in the high-temperature region has possibly been explained by the existence of magnetic polarons near the ferromagnetic transition temperature and their effect on the electron transport with and without an external field.[1,7,14] Here we focus on the low-temperature MR effect. As seen in Fig. 4, below the saturation field (H_s) the resistivity drops rapidly, which is similar to the rapid increase in magnetization. Above the saturation field

the resistivity drops more slowly but still mimics the slow increase in the magnetization. We explain these data based on double exchange between pairs of Mn^{3+} and Mn^{4+} ions. In this mechanism a parallel alignment of the manganese spin is required before electrons can be transferred between the ions [Fig. 5(a)] to give electrical conductivity. Well below T_c, the manganese ions are ferromagnetically ordered and therefore, inside a single magnetic domain the electron transfer between pairs of Mn^{3+} and Mn^{4+} ions is easy. But for an unmagnetized specimen there exist many domains [Fig. 5(b)] which have different magnetization directions.[23] Near the domain-wall boundaries, the pairs of spins of Mn^{3+} and Mn^{4+} may not be parallel. As a result the electron transfer between pairs of Mn^{3+} and Mn^{4+} ions across the domain wall is difficult and the resistivity is high. In a strong enough field, the magnetic domains tend to align along the field direction. As a result electrons are transferred more easily across the domain-wall boundaries and the resistivity decreases.

In addition we can explain the high-field (i.e., $H>H_s$) effect using the double exchange mechanism. The high-field MR effect may have its origin in a small canting of the manganese moments inside each domain since the magnetization increases slightly even for $H>H_s$. For $H>H_s$ the canting angle will become smaller and therefore electrons will transfer more easily between pairs of Mn^{3+} and Mn^{4+} ions. This will lead to a MR effect. This possible explanation is only valid for $T\ll T_c$. Further work is needed to understand this MR effect in depth and over the entire temperature range.

In summary, we studied the electronic and magnetic properties of polycrystalline $La_{0.67}Ba_{0.33}MnO_z$ by reducing oxygen stoichiometry from 2.99 to 2.80. We found a metal-to-insulator transition near an oxygen content of 2.80. We have also found that the resistivity, magnetoresistance, and magnetization behavior of bulk oxygen-deficient $La_{0.67}Ba_{0.33}MnO_z$ is similar to that of films previously reported to have a very large magnetoresistance effect. Therefore we believe the MR effect observed in films of $La_{0.67}Ba_{0.33}MnO_z$ is related to the oxygen deficiency. At low temperature the magnetoresistance was observed to be strongly dependent on the magnetization. We presented a possible explanation using the concept of double exchange between pairs of Mn^{3+} and Mn^{4+} ions.

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[22] We believe that the films previously reported to have a large magnetoresistance are oxygen deficient. In addition to the oxygen deficiency, the degree of crystallinity and uniformity of oxygen distribution contribute to the large MR effect in the films.

[23] For polycrystal samples, the magnetic domain size may be limited by polycrystal size in the sample. We assume that the magnetic domain size is roughly the same as the polycrystal size.