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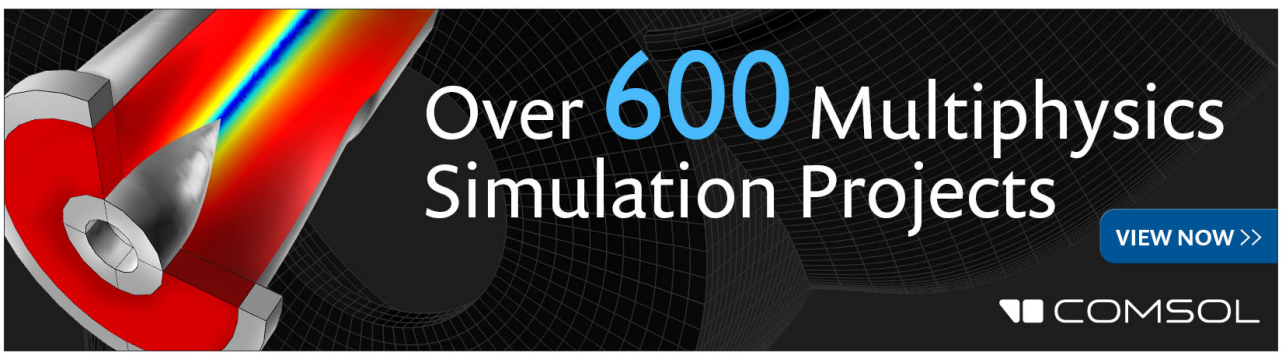

The influence of the antiferromagnetic boundary on the magnetic property of La_2NiMnO_6

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Polycrystalline La_2NiMnO_6 compounds were fabricated at different temperatures and their magnetic properties were investigated. Although the antiferromagnetic antisite disorder degree changes a little, the antiferromagnetic coupling intensity increases with increasing synthesized temperature. When La_2NiMnO_6 sample was cooled at 100 Oe from room temperature to 10 K, exchange bias was observed. Our results confirm that the exchange bias should originate from the coupling between the ferromagnetic La_2NiMnO_6 and antiferromagnetic antiphase boundaries. © *2009 American Institute of Physics*. [doi:10.1063/1.3267053]

The double perovskite oxides ($A_2B'B''O_6$) have attracted much more attention due to their variety of the electrical and magnetic properties.[1–3] The magnetic structure of most double perovskite oxides was described as ferrimagnetic and/or antiferromagnetic due to the antiferrimagnetic coupling between the B′ and B″ ions.[4] But the double perovskite La_2NiMnO_6 (LNMO) is a ferromagnetic semiconductor ($T_C \approx 280$ K), which had been predicted according the Goodenough–Kanamori's rules and been confirmed by the experimental data.[1,2,5] Recently, Rogado *et al.* observed a large magnetocapacitance and magnetoresistance near the Curie temperature in LNMO powders, and suggested that the spin, electric charge, and dielectric can be tuned in LNMO by the magnetic field.[6] It is these features that make LNMO a potential candidate for spintronic devices.

The saturation magnetization per formula unit of LNMO reported so far are much smaller that its theoretical spin-only value of 5 μ_B/f.u., which was attributed to the presence of the antiferromagnetic antisite defect introduced by the partial disorder Ni^{2+} and Mn^{4+} ions between the NiO_6 and MnO_6 sublattices.[1,7] The antisite disorder is a natural growth defect in double perovskite oxides, which strongly influence the magnetic-electric properties of the double perovskite. Goodenough *et al.*[8] further proposed that the antiferrimagnetic antiphase boundaries (APBs) should exist in double perovskite with high antisite degree.[7] The antiferromagnetic APB has been revealed in other double perovskite oxides by transmission electron microscopy and MÖssbauer spectra.[9,10] We also found that the nonmagnetic ion doing in double perovskite Sr_2FeMoO_6 can suppress the formation of the APBs.[11] However, clearer experimental evidences of the existence of the antiferromagnetic APB in LNMO are still lacking.

In this letter, we study the magnetic properties of LNMO polycrystalline samples with high disorder degree. Three samples prepared at different temperatures have same magnetic moment at 10 and 5 T, which shows the same disorder degree in the three samples. But the antiferrimagnetic coupling intensity increases with increasing synthesized temperature, and the exchange bias is observed in LNMO prepared at 1350 °C, which suggests the existence of the antiferrimagnetic APBs in LNMO.

The polycrystalline LNMO samples were prepared by means of a sol-gel method with $La(NO_3)_3 \cdot 6H_2O$, $Ni(NO_3)_2 \cdot 6H_2O$, and $Mn(NO_3)_2$ as the starting materials, and citric acid and ethylene glycol were added in appropriate ratios. The gel was thoroughly fired at about 300 °C, and then calcined in oxygen at 500 °C for 12 h. And then the mixture powder was pressed into pellets and sintered at different temperature for 48 h, respectively. We refer to the samples sintered at 600 °C, 900 °C, and 1350 °C by LNMO-A, -B, and -C, respectively. X-ray diffraction (XRD) powder pattern was collected using the Bede D^1 XRD spectrometer with Ni-filtered Cu $K\alpha$ radiation. The room temperature XRD patterns show that all of the samples are a single double perovskite phase, and agree well with the literatures.[7] The magnetization measurements were carried out using the physical properties measurement system (PPMS) of Quantum Design. In order to obtain a low field, the superconducting magnet of PPMS was demagnetized before measurements.

Figure 1 shows the temperature dependence of the magnetization measured in a magnetic field of 100 Oe after zero-field-cooled (ZFC) and field-cold (FC) processes for the LNMO polycrystalline samples. The ZFC curves of the LNMO-A and -B samples exhibit wide peaks at low temperature. These wide peaks should originate from the superparamagnetism of the LNMO powders, similar with the results of Goodenough *et al.*[7] due to the lower synthesized temperature. Although the magnetization moment decreases with increasing synthesized temperature, all of the ZFC and FC curves separate with each at about 280 K. These results

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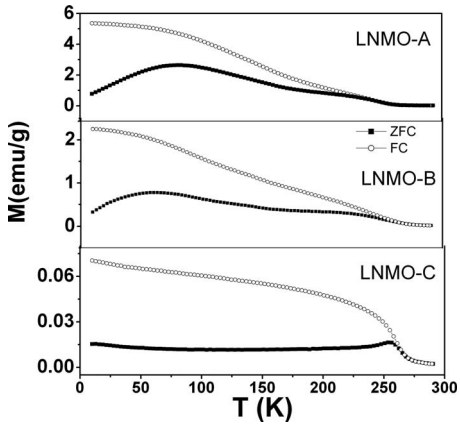

FIG. 1. Temperature dependent magnetization measured in the ZFC and FC processes at 100 Oe field for LNMO samples.

imply that the onset of the ferromagnetic long-range ordering occurs at about 280 K.[6,7]

Figure 2 shows the isothermal magnetization curves of the LNMO samples at 10 K and magnetic field up to 5 T. All of the samples show ferromagnetic behaviors at low temperature. The saturation moments per formula unit (2.2 μ_B/f.u.) at 10 K and 5 T are much lower than the theoretical spin-only value (5.0 μ_B/f.u.) as reported as literatures.[6,7,12,13] It means that the LNMO samples have many antiferromagnetic antisite disorders of $Ni^{2+}-O-Ni^{2+}$ and $Mn^{4+}-O-Mn^{4+}$, and the antisite disorders degree does not change a lot for the three samples. However, the saturated fields are much different for the samples, which suggest that the antiferromagnetic coupling intensity in LNMO-C sample are stronger than that in -A or -B samples. This remarkable increase of antiferromagnetic coupling should be attributed to the formation of the antiferromagnetic APBs in the LNMO-B and -C samples, and the amount of APBs in LNMO-C sample would be much larger than that in -B sample. The LNMO-A sample was prepared at low temperature of 600 °C, and the grain size is very small. So the antisite disorders distribute lonely in each LNMO grain, and there are not strong magnetic coupling among the antisite disorders. With increasing the synthesized temperature, the LNMO grains grow, and many antisite disorders may exist in one grain. So the magnetic coupling among the antisite disorders comes into being. The coupling intensity increases with increasing LNMO grain size, and the antiferromagnetic boundaries will be formed once the threshold achieved.

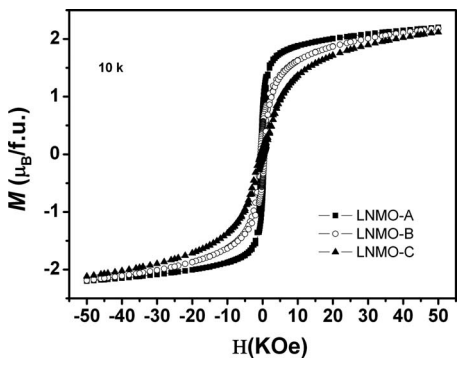

FIG. 2. The magnetization curves of LNMO samples at 10 K and upto 5 T.

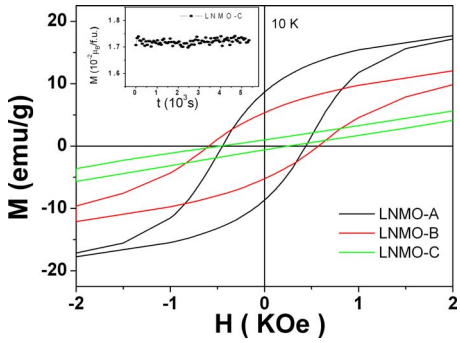

FIG. 3. (Color online) Hysteresis loops of LNMO samples after cooling at 100 Oe from 300 K. Inset shows the time dependent of magnetization M of LNMO-C sample at 100 Oe.

So, there are some ferromagnetic and antiferromagnetic moments in the LNMO samples with high antisite disorder degree. It is well known that an exchange bias will often been observed in heterogeneous system consisting of ferromagnetic and antiferromagnetic spin structure due to the coupling of the ferromagnet and antiferromagnet at the interface when the system is cooled down in an external magnetic field from high temperature (above the Neel temperature of the antiferromagnet) to low temperature.[14,15] Taking into account the low ferromagnetic moment and high antiferromagnetic antisite disorder degree in the LNMO samples, it is more likely that the exchange bias could be expected in all LNMO samples. Therefore, we measured the hysteresis loops of LNMO at 10 K with both ZFC and FC processes. For the ZFC process, normal hysteresis loops that centered at zero fields were observed (not shown). However, for the FC process, when the samples were cooled from 300 to 10 K at 100 Oe and then measured between ±5 KOe, the hysteresis loop of LNMO-A and -B still show normal hysteresis loops, but the exchange bias was observed in LNMO-C sample, as shown in Fig. 3.

The exchange bias was first discovered in ferromagnet Co system coated with an antiferromagnetic CoO layer.[14] Recently, Tang *et al.*[16] also observed the exchange bias in phase-separation $La_{1-x}Sr_xCoO_3$ due to coupling of ferromagnet and spin-glass interface. To further confirm the origination of the exchange bias, the LNMO-C sample was cooled from 300 to 10 K at zero fields. After waiting 1000 s, a dc magnetic field of 100 Oe was applied and the magnetization M was recorded versus time t. Obviously, the magnetic moment did not change any more with increasing measured time, as shown in the inset of Fig. 3, which suggests there isn't spin-glass phase in the LNMO-C sample.[16] Therefore, the exchange bias should origin from the coupling of ferromagnetic LNMO with antiferromagnetic APBs. As analyzed above, many antisite disorders will change into APBs with increasing synthesized temperature. The antiferromagnetic APBs will lead to the antiferromagnetic coupling of the neighboring ferromagnetic regions. When the coupling intensity between the antiferromagnetic APBs and ferromagnetic LNMO reaches the threshold value, the exchange bias is observed.

In summary, we have observed the exchange bias in the double perovskite LNMO samples, which gives strong evidence for the existence of the APBs in double perovskite oxides. The antiferromagnetic APBs may play an important role in the application of LNMO in spintronic devices.

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