RAPID COMMUNICATION

Abnormal magnetic behaviors induced by the antisite phase boundary in La_2NiMnO_6*

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The ferromagnetic semiconductor La_2NiMnO_6 (LNMO) has recently received much attention due to its high Curie temperature ($T_C \sim 280$ K), which is close to room temperature. We prepared single-phase LNMO polycrystalline samples and investigated the temperature- and field-dependent magnetic behaviors of bulk LNMO. Between T_C and $T^* = 300$ K, we observed upward and downward deviations from the Curie–Weiss law for high and low magnetic fields, respectively. From the electron spin resonance results, we can exclude the existence of the Griffiths phase. On the contrary, our results indicate that the abnormal magnetic behaviors might be induced by antisite phase boundaries with antiferromagnetic interaction.

Keywords: antisite phase boundary (APB), La_2NiMnO_6, electron spin resonance (ESR)

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1. Introduction

Magnetic semiconductors were one of the hot research topics in condensed matter physics during the past decade.[1] Recently, the discovery of ferromagnetic (FM) ordering in the La_2NiMnO_6 (LNMO) semiconductor has received much attention, due to its high Curie temperature T_C (~ 280 K).[2] To understand the physical origin of the ferromagnetic transition near 280 K, the magnetic properties of LNMO have been widely investigated over the years.[3–7] LNMO has a typical double perovskite structure with two different B-site ions, as shown in Fig. 1(a). The Ni and Mn atoms in the bulk LNMO sample are usually ordered in terms of B-site occupation, as shown in Fig. 1(b). However, there could be structural domains in which the boundary atoms from different domains are identical, being either Ni or Mn. When two such domains meet, an interface called an antisite phase boundary (APB) is created,[8] containing either Ni–O–Ni or Mn–O–Mn bonds only, as shown in Fig. 1(b). In the fully ordered LNMO, the valence of the Ni and Mn ions are Ni^{2+}/Mn^{4+}, while in the fully disordered $LaNi_{0.5}Mn_{0.5}O_3$ (113 phase), the valences should be Ni^{3+}/Mn^{3+} with different crystal structures. It is generally accepted that Ni^{2+}/Mn^{4+} is dominant, and a small proportion of Ni^{3+}/Mn^{3+} valences coexist in LNMO, depending on the synthesis conditions of the sample.[9] Goodenough originally proposed that the exchange interaction between Mn^{3+} and Ni^{3+} is responsible for the FM transition near 280 K.[10] Later, more and more evidence supported the conclusion that a superexchange interaction between the ordered Ni^{2+} and Mn^{4+} ions causes the ferromagnetic ordering at T_C.[11]

On the other hand, in the case of dominant Ni^{2+}/Mn^{4+} ions, the superexchange of either Ni^{2+}–O–Ni^{2+} or Mn^{4+}–O–Mn^{4+} in APBs is expected to be antiferromagnetic (AFM), based on the Goodenough–Kanamori rule, which posits that neighboring moments are forced to align in an antiparallel way at the APBs.[12] The existence of the AFM interactions in APBs leads to complex magnetic behaviors. Recently, Zhou *et al.*[13,14] observed an upward deviation from the Curie–Weiss (CW) law above T_C in an LNMO polycrystalline sample. After decreasing the grain size to the nanometer scale, an unusual downward deviation from the CW law can also be observed. They argued that the change from upward to downward deviations in their samples is induced by the weakening of AFM interactions arising from APBs in the nano-sized sample. However, the relation between the APBs and the downward deviation is still unclear.

Usually, the downward derivation above T_C is thought to be induced by the so-called Griffiths phase with quenched-disorder FM clusters before the stabilization of fully magnetic ordering.[15,16] Then, the low field magnetic susceptibility usually shows an enhancement above T_C due to the contribution from these FM clusters. M is the magnetic moment with normalized mass. Therefore, it is necessary to further investigate

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the physical origin of the downward derivation behavior found in LNMO.

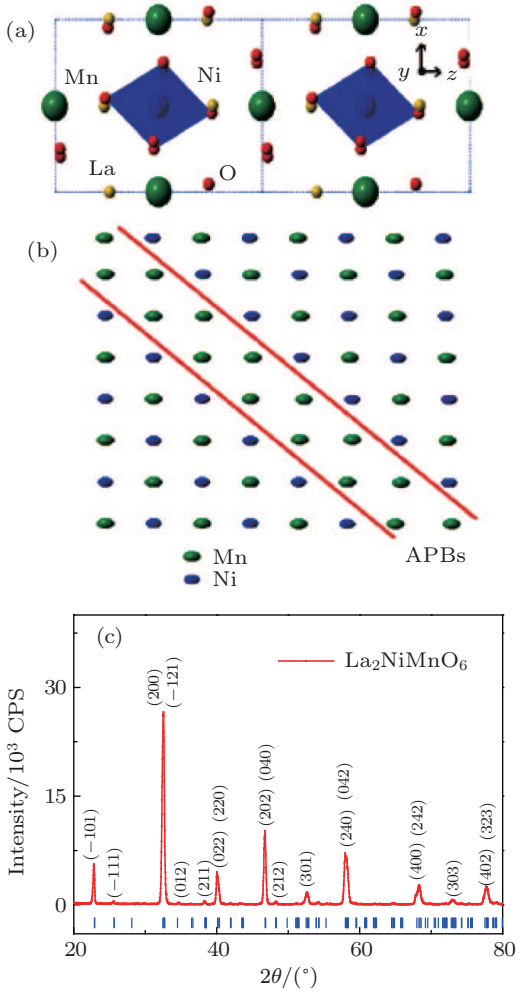


Fig. 1. (color online) (a) Schematic illustration of the crystal structure, (b) the differently ordered domain and antisite phase boundary of La_2NiMnO_6, and (c) the room-temperature powder X-ray diffraction patterns. The vertical bars display the simulated peak positions with the reported lattice parameters.[9]

In the present work, we studied the magnetic properties of a single-phase LNMO polycrystalline sample. An abnormal magnetic behavior was observed between $T^* = 300$ K and $T_C = 275$ K, where the inverse magnetic susceptibility (χ^{-1}) deviates from the CW law, either upward or downward depending on the applied magnetic fields. However, electron spin resonance (ESR) measurements show no trace of FM clusters between T^* and T_C, and they simply follow the CW behavior. Based on these results, we rule out the existence of the Griffiths phase and attribute the APBs as the physical origin of both downward and upward deviations from CW law.

2. Experiments

Polycrystalline La_2NiMnO_6 was prepared with stoichiometric La_2O_3 (99.9%, Aldrich), MnO (99.9%, Aldrich), and NiO (99.9%, Aldrich). The raw materials were first ground and pressed into a pellet. Then the sample was synthesized by a solid-state reaction at 1473 K for 96 h in air followed by a cooling rate of 20 K/h down to room temperature. The room-temperature powder X-ray diffraction pattern was recorded in a Dmax2500-V X-ray diffractometer with Cu Kα radiation ($\lambda = 1.54059$ Å). The sample is confirmed to have a typical pervoskite structure with the monoclinic space group $P2_1/n$. No impurity phase could be detected. The magnetic measurements were carried out with a Verslab (Quantum Design), and the ESR measurements were performed with a JEOL JES-200 spectrometer at the X band (9 GHz).

3. Results and discussions

Figure 1(c) shows the room-temperature powder X-ray diffraction patterns of the La_2NiMnO_6 sample. All the diffraction peaks can be indexed with the monoclinic space group $P2_1/n$, and their position is consistent with the reported values for LNMO.[8] The crystal structure of our sample is different from that of the 113 phase ($LaNi_{0.5}Mn_{0.5}O_3$), indicating the dominant ordering of Ni^{2+}/Mn^{4+} in the specimen. Therefore, one would expect an FM transition near room temperature in our sample.

We measured the temperature (T)-dependent magnetic susceptibility $\chi(T)$ under both the $\boldsymbol{H} = 10^4$ Oe (the unit 1 Oe = 79.577 A·m^{-1}) and $\boldsymbol{H} = 10^3$ Oe with zero field cooling process, as shown in Fig. 2(a). These curves clearly show a ferromagnetic transition at $T_C \sim 275$ K, as expected. Figure 2(b) illustrates the inverse susceptibility (χ^{-1}) against the temperature curves. Well-defined CW behaviors are observed above $T^* = 300$ K for both magnetic fields. Surprisingly, between T_C and T^*, the inverse susceptibility exhibits either a downward or upward deviation from the CW law in $\boldsymbol{H} = 10^3$ Oe and $\boldsymbol{H} = 10^4$ Oe, respectively. Usually, LNMO polycrystalline samples either show an upturn feature for both low and high $\boldsymbol{H}$ or a downturn in a sample with nano-sized grains. An upturn and downturn have never been observed in the same sample. Such a downturn under low H and upturn under high H are characteristic of the Griffiths phase.[15] In this case, the T^* might be considered to be the Griffiths temperature.

To testify the existence of the Griffiths phase in the temperature region $T_C < T < T^*$, we performed ESR measurements with the powder LNMO sample. In general, an FM peak should be observed between T_C and the Griffiths temperature for samples with a Griffiths phase.[17] The ESR curves at different temperatures for our sample are shown in Fig. 3(a). A typical FM peak gradually disappears when the temperature increases from 260 K to 280 K, and above 280 K, a pure paramagnetic peak appears with the g factor very close to 2.

Between T_C and T^*, only paramagnetic peaks can be observed with no trace of FM signals. Moreover, the temperature dependence of ESR intensity I and its inverse $1/I$–T curve are plotted in Fig. 3(b). The I–T curve displays a peak around T_C, indicating the onset of FM transition. Between T_C and 350 K, the $1/I$ versus T curve follows the CW law and there is no obvious anomaly at T^* ($\sim$ 300 K). The above observations clearly indicate that no short-range FM interaction exists above T_C. Therefore, we can conclude that the Griffiths phase does not exist in our specimen and the deviation of CW behavior below T^* must have another physical origin.

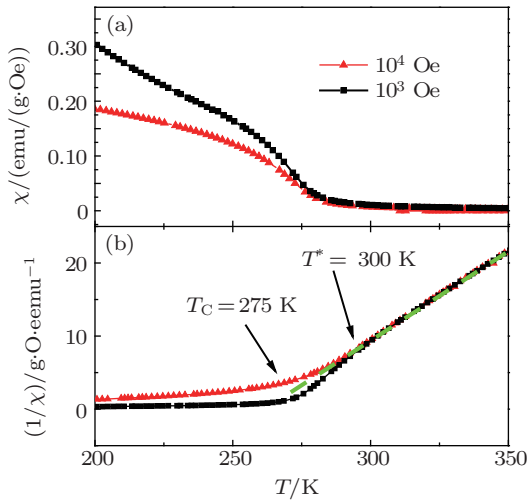


Fig. 2. (color online) The temperature dependence of (a) magnetic susceptibility $\chi(T)$, and (b) inverse magnetic susceptibility (χ^{-1}) in low (10^3 Oe) and high (10^4 Oe) magnetic fields.

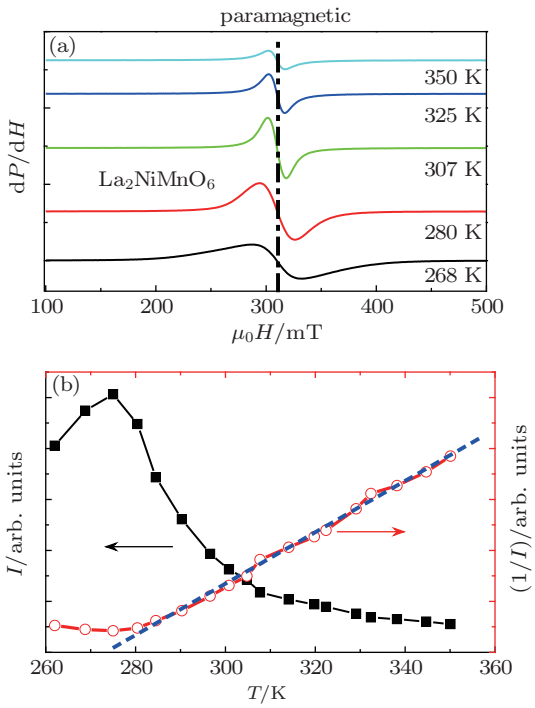


Fig. 3. (color online) (a) The ESR spectra of LNMO at different temperatures, and (b) the temperature dependence of ESR intensity (I) and its inverse ($1/I$) for La_2NiMnO_6. The dashed-dotted line in (a) indicates the paramagnetic peak positions.

Figure 4 displays the M–H curves at 55 K (below T_C) and 300 K (at T^*). The typical paramagnetic behavior was observed at 300 K. At 55 K, the sample shows an FM hysteresis loop, and the nearly saturated magnetization of the sample was about 2.3 μ_B/f.u., which is much smaller than the theoretical value 5 μ_B/f.u. ($Ni^{2+}: t_{2g}^6 e_g^2$ and $Mn^{4+}: t_{2g}^3 e_g^0$). This much smaller saturation magnetization has appeared in many LNMO samples[9] and has been thought to come from the APBs, since it can result in an AFM alignment between neighboring Ni/Mn occupation domains. Thus, the APBs should also exist in our sample due to the significant reduction in saturation moment.

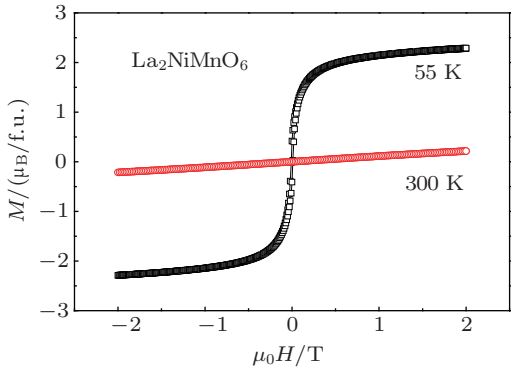


Fig. 4. (color online) The M–H curves of La_2NiMnO_6 at 55 K and 300 K.

Here, we would like to discuss the relationship between APB and the deviation of CW behavior below T^* in our LNMO. Actually, some reports already attribute the upward deviation from the CW behavior of LNMO to the AFM interaction in APBs above T_C. This deviation does not conflict with our ESR results because the AFM Ni^{2+}–O–Ni^{2+} and Mn^{4+}–O–Mn^{4+} couplings do not contribute to the ESR signal. In terms of downward deviation behavior, it has exactly the same character temperature, T^*, as that of the upward one, and should have a similar physical origin as well. Goodenough *et al.* previously observed a similar magnetic susceptibility behavior in another double-perovskite compound $Sr_{2-x}Ca_xFeMoO_6$, and proposed that its downward deviation can also be induced by APB at low fields.[8] The existence of such APB interfaces would, at zero field, have an antiparallel coupling to the ferromagnetic domains on opposite sides of the interface. Since the volumes of the two different types of domain would not be equal, there would be a residual magnetization, which leads to the enhancement of susceptibility at zero field. The enhancement of susceptibility can still be observed in low fields, while all ferromagnetic domains will align in parallel when a larger field is applied. Then, the susceptibility will decrease after the sample reaches saturation. It can be

confirmed that APB is a non-random disorder[8] that behaves differently from either the Griffiths phase with quenched random disorder or short-range FM ordering. The relative orientation (parallel or antiparallel) of the magnetization across the APBs depends on the applied magnetic fields, and thus gives rise to the peculiar behavior of magnetic susceptibility.

4. Conclusions

In conclusion, we have investigated the temperature- and field-dependent magnetic behaviors of bulk La_2NiMnO_6 around T_C. Surprisingly, between $T^* = 300$ K and $T_C = 275$ K, the inverse magnetic susceptibility (χ^{-1}) deviates from the CW law, either upward in high magnetic fields or downward in low magnetic fields. However, ESR measurements show no trace of FM clusters between T^* and T_C, and rule out the existence of the Griffiths phase. Instead, we attribute the abnormal magnetic behaviors to the field-dependent interaction at the APBs.

References

[1] Liu X C, Zhang H W, Zhang T, Chen B Y, Chen Z Z, Song L X and Shi E W 2008 *Chin. Phys. B* **17** 1371

[2] Rogado N S, Li J, Sleight A W and Subramanian M A 2005 *Adv. Mater.* **17** 2225

[3] Guo H, Gupta A, Varela M, Pennycook S and Zhang J 2009 *Phys. Rev. B* **79** 172402

[4] Sanyal P and Majumdar P 2009 *Phys. Rev. B* **80** 054411

[5] Singh M, Truong K, Jand S and Fournier P 2009 *Phys. Rev. B* **79** 224421

[6] Das H, Waghmare U, Saha-Dasgupta T and Sarma D 2009 *Phys. Rev. B* **79** 144403

[7] Truong K, Singh M, Jand S and Fournier P 2009 *Phys. Rev. B* **80** 134424

[8] Goodenough J B and Dass R 2000 *Int. J. Inorg. Mater.* **2** 3

[9] Dass R I, Yan J Q and Goodenough J B 2003 *Phys. Rev. B* **68** 064415

[10] Goodenough J B, Wold A, Arnott R J and Menyuk N 1961 *Phys. Rev.* **124** 373

[11] Sonobe M and Asai K 1992 *J. Phys. Soc. Jpn.* **61** 4193

[12] Singh V N and Majumdar P 2011 *Europhys. Lett.* **94** 47004

[13] Zhou S, Shi L, Yang H and Zhao J 2007 *Appl. Phys. Lett.* **91** 172505

[14] Zhou S M, Guo Y Q, Zhao J Y, Zhao S Y and Shi L 2010 *Appl. Phys. Lett.* **96** 262507

[15] Griffiths R B 1969 *Phys. Rev. Lett.* **23** 17

[16] Bray A J 1987 *Phys. Rev. Lett.* **59** 586

[17] Deisenhofer J, Braak D, Krug von Nidda H A, Hemberger J, Eremina R M, Ivanshin V A, Balbashov A M, Jug G, Loidl A, Kimura T and Tokura Y 2005 *Phys. Rev. Lett.* **95** 257202