

Probability of double exchange between Mn and Fe in $\text{LaMn}_{1-x}\text{Fe}_x\text{O}_3$

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The magnetism and transport properties of heavily doped perovskite $\text{LaMn}_{1-x}\text{Fe}_x\text{O}_3$ ($0.00 \leq x \leq 0.40$) were studied. For the doped samples, there is a paramagnetic–ferromagnetic (PM–FM) transition both under zero field cooling and 0.01 Tesla field cooling condition but there is no insulator–metal transition. The curves are fitted well by the thermal activation model. The Mössbauer spectra of heavily doped samples demonstrate that the doped Fe ions are trivalent. In electron spin resonance spectra, many individual ferromagnetic resonance lines occur besides the normal paramagnetic resonance lines at $T > T_C$ and then submerge in PM or FM lines at low temperature. We suggest that there is the probability of double exchange interaction between Fe^{3+} ions and Mn^{3+} ions in $\text{LaMn}_{1-x}\text{Fe}_x\text{O}_3$.

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I. INTRODUCTION

As we know, the LaMnO_3 is an antiferromagnetic (AFM) insulator with ABO_3 perovskite structure. In the LaMnO_3 system the Mn ions are all trivalent and there exists superexchange (SE) interaction in $\text{Mn}^{3+}\text{--O--Mn}^{3+}$. The studies of doping are mainly focused on $\text{La}_{1-x}\text{A}_x\text{Mn}_{1-y}\text{B}_y\text{O}_3$ ($x = 1/3$; $\text{A} = \text{Ca, Sr, Ba, Pb}$; $\text{B} = \text{Fe, } ^1\text{Cr, } ^2\text{Ga, } ^3\text{Co, } ^4\text{Al}^5$). When La ions are substituted by divalent alkaline earth ions, based on the balance of valence, the same proportion of Mn^{3+} will be transformed to Mn^{4+} , and there appears paramagnetic–ferromagnetic (PM–FM) transition accompanied with insulator–metal (IM) transition in this system, which was explained by double exchange (DE) interaction⁶ between Mn^{3+} and Mn^{4+} and Jahn-Teller distortion.^{7,8} In recent reports, the substitution of magnetic ions for Mn ions in $\text{La}_{0.7}\text{A}_{0.3}\text{MnO}_3$ and LaMnO_3 has been extensively performed. Such as, Sugantha *et al.* studied the substitution of Fe and Cr for Mn ions in $\text{La}_{0.7}(\text{Sr}/\text{Ca})_{0.3}\text{MnO}_3$ and indicated that the PM–FM transition is accompanied with IM transition, but the IM transition temperature decreases with the increase in x .⁹ While by the substitution of the Mn site in LaMnO_3 , there is always the PM–FM transition but no IM transition, which has been explained by many authors.^{10–15} For example, Yang *et al.*¹⁶ indicated that the crystal lattice distortion caused by doping is helpful to open up the band gap in $\text{LaMn}_{1-x}\text{Co}_x\text{O}_3$. The gap would suppress charge ordering, so there is no IM transition. However, there are many ideas about the mode of coupling between Mn ions and doped B ions. Goodenough *et al.*¹⁰ suggested that there exist ferromagnetic superexchange interaction between Mn^{3+} and B ions ($\text{B} = \text{Ni}^{3+}, \text{Co}^{3+}$) in $\text{LaMn}_{1-x}\text{B}_x\text{O}_3$. In fact, Asai *et al.*¹¹ indicated that ferromagnetic superexchange interaction is found between Mn^{4+} and B ions ($\text{B} = \text{Ni}^{2+}, \text{Co}^{2+}$), and Troyanchuk *et al.*¹⁷ suggested that there is the SE interaction between Mn^{3+} and Co^{2+} .

In our experiments, we choose LaMnO_3 as the parent compound to dope Fe instead of $\text{La}_{0.7}\text{A}_{0.3}\text{MnO}_3$ systems. This is based on the following consideration. In LaMnO_3 , the La–O layer is homogeneous without other cations which would cause random Coulomb potential. Thus, it would

eliminate other complex ingredients so that the effect of magnetic ions like Fe can be prominent. Fe ions and Mn ions are all magnetic ions, and Fe^{3+} own high and low spin states whose radii are very similar to those of $\text{Mn}^{3+}/\text{Mn}^{4+}$, respectively. It is worth studying whether there exists the coupling between Mn ions and Fe ions.

II. EXPERIMENTAL DETAILS

The samples were prepared by the conventional solid-state reaction method. The starting materials, La_2O_3 (preheated at temperature of 400–600 °C at first), MnO_2 , Fe_2O_3 , were mixed uniformly and then heated at 800 °C for 12 h, 1000 °C for 12 h, 1200 °C for 12 h with intermediate grinding. Then they were pressed into slices and sintered at 1250 °C for 24 h.

The x-ray diffraction (XRD) was carried out with Rigaku D/Max- γ A rotating powder diffractometer operated with graphite monochromator and using $\text{Cu } K_\alpha$ radiation ($\lambda = 0.1542$ nm). The temperature dependence of magnetization M - T under both zero field cooling (ZFC) and 0.01 Tesla field cooling (FC) condition was measured by a LakeShore 9300 vibrating sample magnetometer (VSM). The temperature dependence of resistivity (ρ - T) both under ZFC and 6 Tesla FC was measured by the standard four-contact method with an Oxford 15 T system. The micromagnetic properties of samples were observed by the measurements of electron spin resonance (ESR) spectra on a Bruker ER200D spectrometer.

III. RESULTS AND DISCUSSIONS

A. Structure and valence state

The x-ray diffraction patterns in Fig. 1 indicate that all of the samples are single phase and the structure of samples changes from rhombohedral ($0.00 \leq x \leq 0.30$) to orthorhombic ($x = 0.40$).

Mössbauer spectroscopy was measured to study the valence of doped Fe ions. The isomer shift presented by Fig. 2 is 0.32–0.34 mm/s, indicating that the Fe ions are all in the trivalent state,¹⁸ so the Fe cannot bring additional tetravalent Mn ions. The fact of trivalent Fe ions and x-ray diffraction

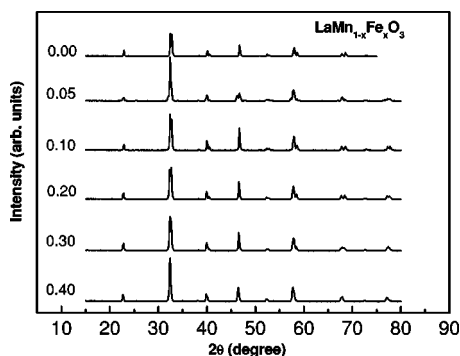


FIG. 1. X-ray-diffraction patterns of $\text{LaMn}_{1-x}\text{Fe}_x\text{O}_3$ ($0.00 \leq x \leq 0.40$).

patterns demonstrate that the samples are single phase, so the Fe ions must have been doped into LaMnO_3 completely and form FeO_6 octahedron together with MnO_6 .

B. Magnetism and conductivity

The M - T curves measured under both ZFC and 0.01 Tesla FC are shown in Fig. 3. The T_c^{onset} is defined as the temperature corresponding to the crossing point of the PM line and tangent line on the PM-FM transition region. We calculated the transition width ΔT by subtracting the temperature corresponding to the maximum of M under ZFC from T_c^{onset} . The T_c^{onset} and the ΔT were listed in Fig. 3. In Fig. 3(a), for $x=0.00$, there is a steep PM-FM transition at $T_c=240$ K and the typical FM state appears at $T < 200$ K. In Figs. 3(b)–3(f), the PM-FM transition appears at low temperature for all Fe-doped samples, but the ZFC M - T curves are very different from FC ones, and they exhibit a λ transition, which means that the cluster-spin glass states are formed. The T_c decreases with doping level increasing. It is very strange that with the increase of Fe content the transition widths ΔT become narrower, instead of wider in other $\text{LaMn}_{1-x}\text{B}_x\text{O}_3$ ($\text{B} = \text{Zn}, \text{Cu}, \text{etc.}$) system. These strange phenomena of magnetism must affect the transport properties of samples.

Comparing Figs. 3(b)–3(f) with (a), we can find that the system $\text{LaMn}_{1-x}\text{Fe}_x\text{O}_3$ is much different from the $\text{LaMnO}_{3+\delta}$. This clearly shows the doping of Fe dominates the system $\text{LaMn}_{1-x}\text{Fe}_x\text{O}_3$ more greatly than the excess of oxygen.

In Fig. 4(a), for $x=0.00$, there is an IM transition at T_c indicated in Fig. 3(a). However, for other doped samples with $x=0.05, 0.10, 0.20, 0.30,$ and 0.40 , the semiconducting behavior is observed and there is no IM transition. It is very common that there is a PM-FM transition but no IM transition in $\text{LaMn}_{1-x}\text{B}_x\text{O}_3$ in the past studies. However, as described in the introduction, the explanation of this effect is not very clear.

Figure 5 shows the ESR spectra at various temperatures for $x=0.05, 0.10, 0.20,$ and 0.30 . The symbol “ Δ ” marks the resonance center of PM line with $g \sim 2$, “ \uparrow ” marks the position of the FM resonance line. We can find that the starting temperature of the appearance of FM line is in accordance with the T_c^{onset} in Fig. 3. It is also seen that there clearly exist PM lines and FM lines for $x=0.05$ and 0.10 , while for $x=0.20$ and 0.30 , there is no such significant sign.

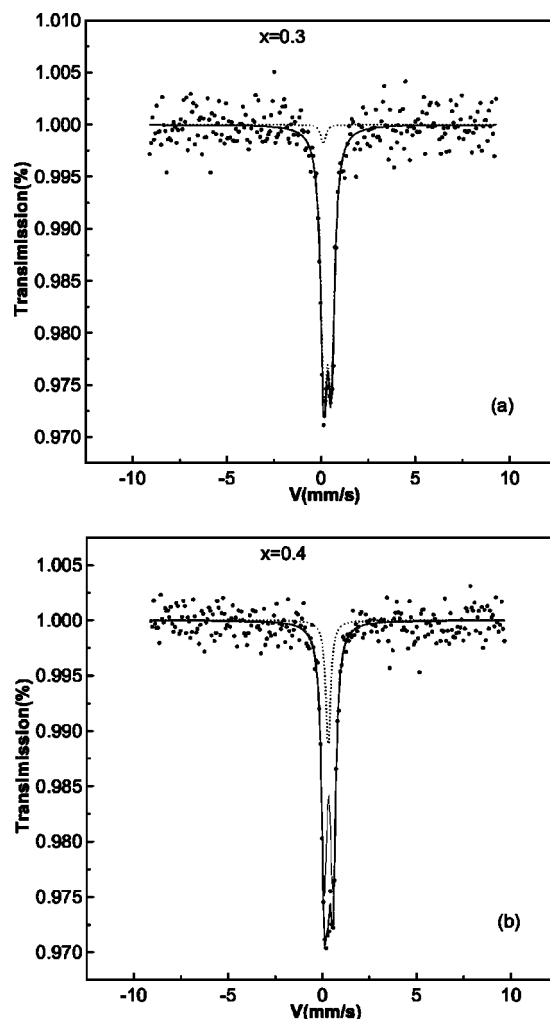


FIG. 2. Room temperature Mössbauer spectroscopy for $\text{LaMn}_{1-x}\text{Fe}_x\text{O}_3$ with $x=0.30$ and 0.40 . Solid circles are experimental points. Dotted lines indicate each of the components used to fit the spectra and solid lines correspond to the total fitted spectra.

This implies the fact that the PM-FM transition becomes sharper indeed with increasing dopant, which is consistent with the M - T curves in Fig. 3.

It is very surprising that there appear to be some individual ferromagnetic resonance lines ($g > 2$) in Figs. 5(b) and 5(c), and 5(d) on the high-temperature PM lines. In Fig. 6, we magnified these ESR spectra for the samples with $x = 0.10, 0.20,$ and 0.30 . It is clear that these individual lines are strengthened gradually relative to the PM lines with increasing temperature, and with decreasing temperature, they submerge into PM or FM lines. Moreover, the number of individual lines is reduced with increasing Fe content, and for $x=0.30$, there is only one wide resonance on the left-hand side of the 3400 G PM line.

C. Probability of DE between Mn^{3+} and Fe^{3+}

In our experiment, there are two notable things. At first, what is the reason of PM-FM transition in $\text{LaMn}_{1-x}^{3+}\text{Fe}_x^{3+}\text{O}_3$ ($x \neq 0$)? Second, why are there PM-FM transitions but no IM transitions?

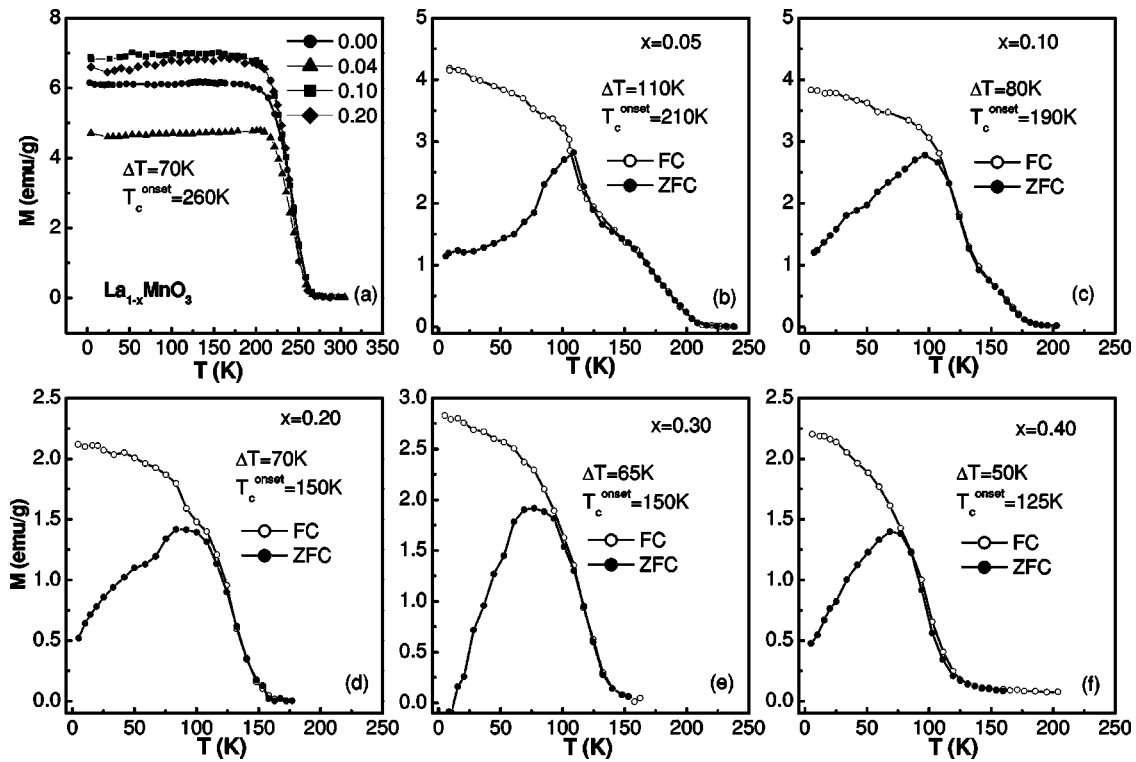


FIG. 3. Temperature (T) dependence of magnetization (M) under zero field cooling (ZFC) and field cooling (FC). (a) For $\text{La}_{1-x}\text{MnO}_3$, (b)–(f) for $\text{LaMn}_{1-x}\text{Fe}_x\text{O}_3$ ($0.05 \leq x \leq 0.40$).

As we know, the end compound LaMnO_3 obtained under normal conditions is often $\text{LaMnO}_{3+\delta}$. In view of the crystal lattice structure, it will be impossible for the additional O atom in the interstice, so in fact, the $\text{LaMnO}_{3+\delta}$ samples should be renamed with $\text{La}_{1-x}\text{Mn}_{1-y}\text{O}_3$,^{19–23} in other words,

there are La/Mn deficiencies. Based on the balance of valence, some of the Mn^{3+} ions will be transformed to Mn^{4+} ions, then the DE interaction between Mn^{3+} and Mn^{4+} will result in the PM–FM transition. In fact, we prepared a series of La-deficient samples $\text{La}_{1-x}\text{MnO}_3$ in air by the same pro-

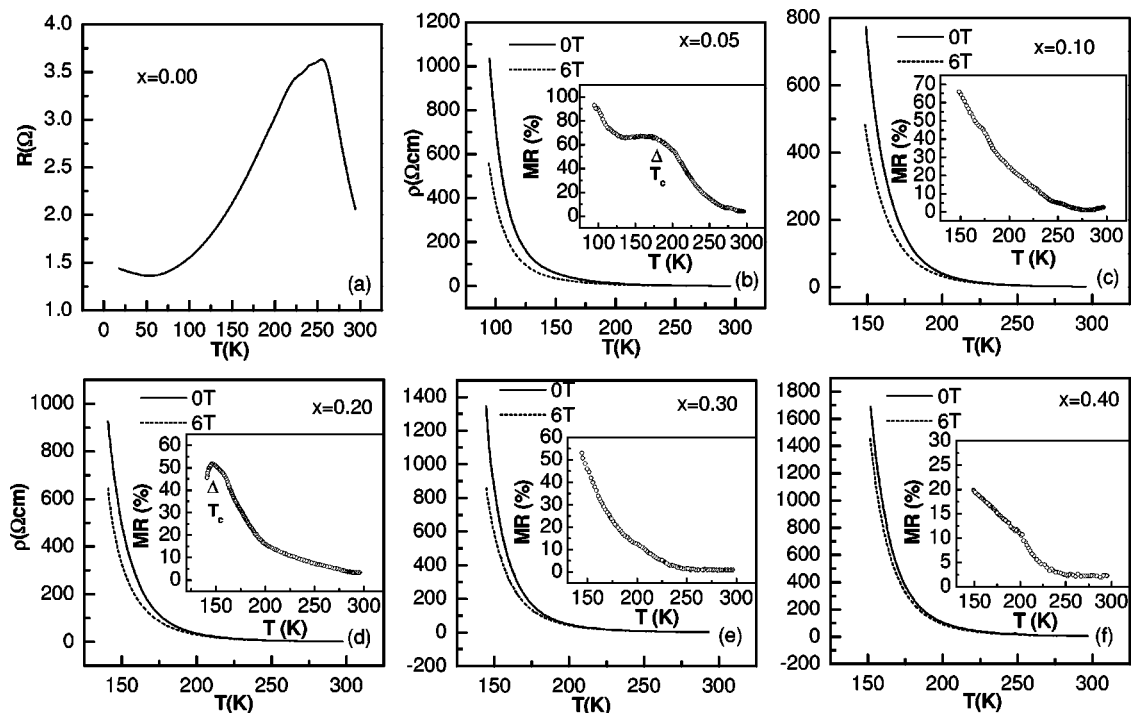


FIG. 4. Temperature (T) dependence of resistivity (ρ) for $\text{LaMn}_{1-x}\text{Fe}_x\text{O}_3$ ($0.00 \leq x \leq 0.40$). The MR results are shown in the inset.

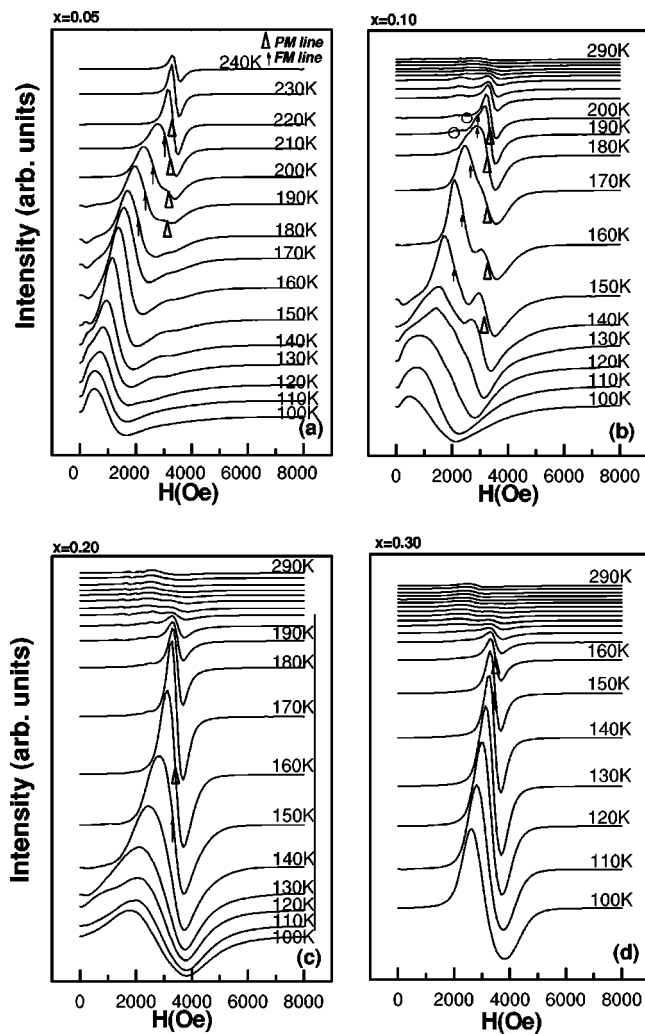


FIG. 5. ESR spectra of $\text{LaMn}_{1-x}\text{Fe}_x\text{O}_3$ with $x = 0.05, 0.10, 0.20,$ and 0.30 at various temperatures.

cedure. Their M - T results show typical FM features whose T_C are not changed with $x < 0.20$ [the inset of Fig. 3(a)], and at the T_C , ρ - T curves exhibit IM transition [shown in the inset of Fig. 4(a) for $x=0.00$]. The results adequately suggest that less than 10% La deficiency in the $\text{La}_{1-x}\text{MnO}_3$ system causes sufficient DE interaction among $\text{Mn}^{3+}-\text{O}-\text{Mn}^{4+}$, which dominates the system behavior of magnetism and transport. However, in our current investigated $\text{LaMn}_{1-x}\text{Fe}_x\text{O}_3$ system, the effect of Fe doping is significant, and absolutely differs from the results caused by the La deficiency.

So, in our Fe doped samples, the PM-FM transition cannot be attributed to the excess of oxygen entirely. (1) If the Fe doping does not change the number of vacancies, the Fe^{3+} would not bring other Mn^{4+} and the total percentage of Mn^{4+} would be fixed in $\text{LaMn}_{1-x}\text{Fe}_x\text{O}_3$. The Fe doping would gradually destroy the DE interaction of $\text{Mn}^{3+}-\text{O}-\text{Mn}^{4+}$, causing formation of the spin cluster. Hence, the transition width would become wider with the increase of doping. However, this is in contradiction to our experimental results. (2) If the Fe doping induces deficiency, the magnetism due to DE would increase, so the T_C would rise. However, this case is in contradiction to experimental results, too. (3) If the Fe doping reduces deficiency, the number of $\text{Mn}^{3+}-\text{O}-\text{Mn}^{4+}$ would decrease. Then the $\text{Mn}^{3+}-\text{O}-\text{Mn}^{4+}$ clusters would become smaller and tend to be consistent with each other. Therefore, the T_C would shift to lower temperature and the width of transition would become narrow. Meanwhile, the carriers among the $\text{Mn}^{3+}-\text{O}-\text{Mn}^{4+}$ clusters are hindered by Fe^{3+} , so there is no IM transition, showing semiconducting behavior. This scenario seems correct, but it cannot interpret the ESR results.

Both the 3d energy level of Fe^{3+} and that of Mn^{3+} are not closed shell, and there are unpaired electrons. Therefore, the resonance lines may be observed by ESR

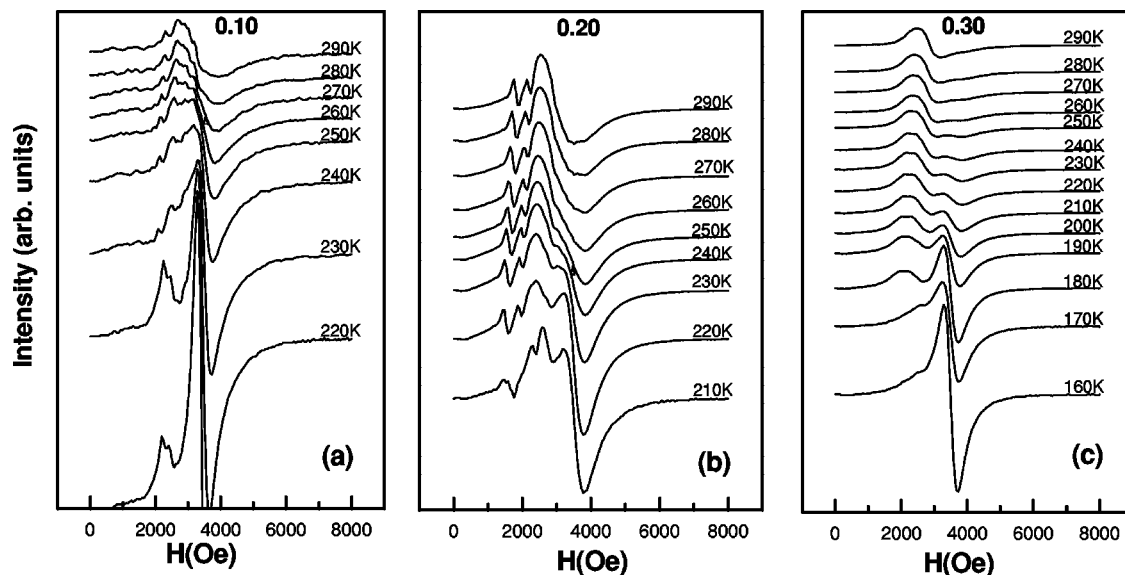


FIG. 6. ESR at high temperature for $\text{LaMn}_{1-x}\text{Fe}_x\text{O}_3$ with $x=0.10, 0.20,$ and 0.30 .

spectra. Compared with the $x=0.05$ sample and previous results,²⁴ it can be determined that the individual resonance lines with $g > 2$ must be caused by Fe^{3+} . When the concentration of Fe ions is low, the distribution of Fe ions is inhomogeneous, in other words, the magnetic environment of Fe ions differs from each other, such as $\cdots\text{Mn}^{3+}-\text{O}-\text{Fe}-\text{O}-\text{Mn}^{4+}\cdots$, $\cdots\text{Mn}^{3+}-\text{O}-\text{Fe}-\text{O}-\text{Mn}^{3+}\cdots$, etc. Therefore, when the samples are scanned by magnetic field, these individual Fe ions will take part in resonance, and so, many individual lines appear. The distribution of Fe ions in lattice will become more homogeneous with the concentration of Fe ions increasing, so these individual FM lines will congregate together for $x=0.20$ and form only a wide single FM line for $x=0.30$. These individual FM lines are weakened and then submerge in PM or FM lines with decreasing temperature, implying that there must be ferromagnetic coupling between Fe ions and Mn ions at low temperature. Otherwise, these individual lines would exist until low temperature, and with temperature decreasing, their strength would increase due to the thermal noise decreasing.

Now, the problem is what kind of interaction causes the FM coupling, superexchange or DE mechanism? In view of electronic structure, Fe^{3+} has five 3D electrons, so it may have three kinds of spin states: (1) $t_{2g}^3e_g^2$, $S=5/2$; (2) $t_{2g}^4e_g^1$, $S=3/2$; (3) $t_{2g}^5e_g^0$, $S=1/2$. A relatively weak crystal lattice field will result in higher spin. But there is no accurate conclusion about the spin state of Fe^{3+} in perovskite. Despite this, both the superexchange and DE interaction are possible. Through the measurement of infrared spectra, we find the absorption peak at 400 cm^{-1} due to the bending mode²⁵ shifts to a little high frequency. This implies the MnO_6 octahedrons are affected with the incorporation of Fe ions, which is also evidenced by x-ray diffraction results (rhombohedral to orthorhombic structure transition). As we know, the radius of low-spin Fe^{3+} is similar to that of Mn^{4+} (69 pm, 67 pm), and the one of high-spin Fe^{3+} nearly equals that of Mn^{3+} (78.5 pm, 78.5 pm). Thus, the Fe^{3+} should exist in low-spin state. So, the e_g level owns empty orbits and the DE will possibly happen. Furthermore, from Fig. 4, we can see there exist significant MR effects for all of the Fe-doped samples and the MR peaks correspond to the PM-FM transition temperature in $M-T$ curves for samples $x=0.05, 0.10$, and 0.20 . For samples with $x=0.30$ and 0.40 , the resistance is so large that it is over the measurement range above the PM-FM transition temperature. As we know, this MR result is consistent with a typical $\text{Mn}^{3+}-\text{O}-\text{Mn}^{4+}$ DE system and generally the superexchange interaction in the perovskite system dominates FM insulator properties without MR effect. So, the DE interaction is favored to exist between $\text{Fe}^{3+}-\text{O}-\text{Mn}^{3+}$. For the probability of DE interaction between Fe and Mn, it is most suitable that the spin state of Fe^{3+} is the second case with $S=3/2$. Thus, the electron can stay at the e_g state with transferring ability for exchange interaction, otherwise, the five 3D electrons would incorporate with a transferred electron forming a localized half-filled t_{2g} state due to the strong Hund's coupling.

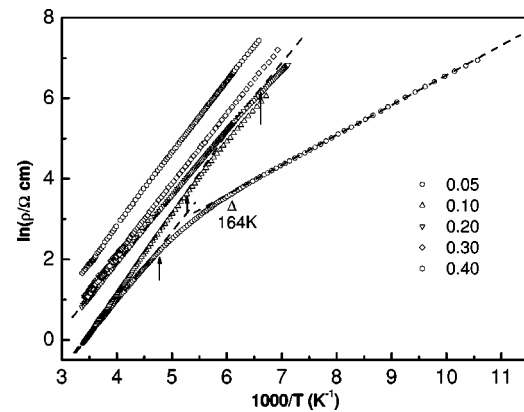


FIG. 7. Resistivity fits to the relation $\rho \sim \exp(E/kT)$ for $\text{LaMn}_{1-x}\text{Fe}_x\text{O}_3$. The arrow lines indicate T_C .

When the DE between Mn and Fe is suggested, the above strange phenomena can be explained well. With the increasing of Fe doping, the $\text{Mn}^{3+}-\text{O}-\text{Fe}^{3+}$ clusters increase and become more consistent with each other. The transition temperatures of the clusters will become more accordant, as a result, the ΔT becomes narrow. At the same time, the relative small Fe ions decrease the bond angle of $\text{M}-\text{O}-\text{M}$, and weaken the DE interaction, resulting in the reduction of T_C .

In Fig. 7 we plotted the $\ln \rho - T^{-1}$ ($0.05 \leq x \leq 0.40$) curves. It can be seen that the resistivity data are fitted well by the thermal activation model. Especially, the curves are divided into two straight lines by T_C . This is because, the Jahn-Teller distortion disappears below T_C , while the contortion of octahedron induced by Fe and the energy different between Fe^{3+} and Fe^{3+} can still exist until low temperature.

IV. CONCLUSION

The x-ray diffraction patterns and Mössbauer spectra of $\text{LaMn}_{1-x}\text{Fe}_x\text{O}_3$ ($0.00 \leq x \leq 0.40$) indicate that all of the samples are single phase and Fe ions are trivalent. The $M-T$ curves for doped samples show a cluster-spin glass state. It is very strange that with Fe dopant increasing the transition widths ΔT become narrow, instead of wide. There is a PM-FM transition but no IM transition. In the ESR spectra, many individual FM lines caused by Fe ions are found at the high temperature region. With temperature decreasing, they submerge in FM or PM lines, then the system enters the FM state. The ESR spectra indicate that there is ferromagnetic coupling between Fe and Mn. We suggest that it can be the DE interaction between Fe ions and Mn ions, and Fe^{3+} may be at $e_{2g}^4e_g^1$ state.

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