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THE EFFECT OF Fe DOPING ON $LaMnO_3$

Y.MIWA, A.YAMAMOTO, K.ODA and H.OTSUKA*

Institute of Industrial Science, University of Tokyo, 7-22-1 Roppongi, Minato-Ku, Tokyo 106-8558
Fax:81-3-3402-6350, e-mail:miwa@cc.iis.u-tokyo.ac.jp
*National Research Institute for Metals, 3-13 Sakura, Tsukuba-Shi,Ibaraki 305-0003

Magnetic and electric properties of $LaMnO_3$ with Mn sites doped with Fe^{3+} ions are investigated. The purpose of the study is to generate giant magnetoresistance(GMR) effect by Fe doping on Mn sites and to clarify the effect of electric and magnetic properties on the GMR effect. Moreover, $^{57}Fe^{3+}$ doped samples are prepared in order to clarify the short range structure around the Mn sites by Mössbauer spectroscopy.

$LaMn_{1-y}Fe_yO_3$ oxides show GMR effect, and the values of $(\rho_0-\rho_H)/\rho_0$ increase as decreasing the temperature. The oxides are ferromagnetic at low temperature and the Curie temperatures are around 190K(dependent on it's composition). Results from Mössbauer spectroscopy show that there are two ferromagnetic sites and one paramagnetic site in Mn sites at low temperature. Internal magnetic field at the Mn sites and the ratio of magnetic sites become smaller as increasing the temperature.

Key words:GMR, perovskite, Mössbauer

1.INTRODUCTION

Lanthanum manganese oxides are known to show negative Giant Magnetoresistance(GMR) effect.[1-11] GMR materials show high sensitivity to magnetic field, so they are used for magnetic sensors, especially for reading heads of harddisks. Present GMR heads are made of metallic multilayers, however the processing of the metallic multilayers is relatively complicated and furthermore, the stability of the films are low. It also requires laborous thin film technique to produce multilayers and the problem of oxidation is serious. On the other hand, perovskite type GMR materials don't need artificial structure like multilayers and they are very stable chemically and thermally, therefore they are easy to deal with. Moreover, some of them show larger GMR effects than metallic multilayers. From these reasons, this category of oxides is now investigated extensively, not only from the physical point of view, but also from the application side.

The series of $La_{1-x}A_xMn_{1-y}B_yO_3$(A,B=metal ions) shows large negative giant magnetoresistance(GMR) effect. These oxides have a perovskite crystalline structure and their electric conductivity originates from the double exchange interaction between neighboring Mn sites. GMR effect can be explained by the spin dependent electron scattering due to the hole transfer through $Mn^{3+}/O^{2-}/Mn^{4+}$.[12] Large GMR effect is observed in samples with rhombohedral crystalline structures in which the angle of $Mn^{3+}/O^{2-}/Mn^{4+}$ is close to 180 degree.

La-Mn oxide systems with various dopant are studied about their structures, electrical and magnetic properties. But almost all of them are about the oxides with La site doping, and only few studies about samples with transition metal ions doped into Mn site exist.[13-14] In this paper, Fe doped La-Mn oxide samples are prepared and investigated about their electric and magnetic properties.

Moreover, there are many studies about long range or middle range ordering of perovskite structure but short range structure are scarcely dealed with, so we clarified hyperfine structure around Fe^{3+} ion at Mn site by Mössbauer spectrum.

2.EXPERIMENTAL

To investigate GMR effect and magnetic properties of Fe doped samples, we prepared samples with the composition of $LaMnO_3$ and $La(Mn_{1-x}Fe_x)O_3$ (x=0.01,0.03,0.05,0.10) by conventional solid state reaction method. We also prepared a Ca doped sample, $(La_{0.90}Ca_{0.10})MnO_3$, for comparison. La_2O_3, MnO_2, $^{57}Fe_2O_3$, $CaCO_3$ powder was mixed with proper ratio for more than 2 hours, pressed into pellets, calcined in air at 1223K for 12 hour. In the case of La_2O_3, for the purpose to dehydrate $La(OH)_3$ completely into La_2O_3, the powder was heated in a vacuum and then sealed in a glass tube. The pellets were ground for 2 hours, pressed again, sintered in air at 1243K for 18 hours.

The phases of prepared samples were identified by X-ray powder diffraction. Temperature dependence of magnetization (M-T curves) and magnetic field dependence (M-H curves) at several temperatures were measured by Vibrating Sample Magnetometer(VSM). M-T curves were measured with applying the magnetic field of 0.1T. Electric resistivity in magnetic field at room temperature and low temperatures were also measured. Temperature was set every 20 K from 300K to 20K. Magnetic field was set every 0.5T from +5T to -5T (every 0.1T from +1T to -1T). Resistivity were measured by four probe method, and current direction was parallel to magnetic field.

From the measurements of the compositions by Inductively Coupled Plasma spectrometry(ICP), we noticed that La-Mn oxides tend to be peroxide, so we tried to deoxidize the Fe 3% sample by annealing in N_2 gas at 1373K.

Mössbauer spectra of $La(Mn_{0.97}Fe_{0.03})O_3$ sample annealed in N_2 (annealed Fe 3% doped sample) were

measured from 81K to 173K and at room temperature by transmission γ -ray method. γ -ray source was ^{57}Co, and the velocity was calibrated by α -iron.

3.RESULTS

3.1 X-ray diffraction

X-ray diffraction patterns of the produced samples are shown in Fig.1. All samples are perovskite single phase. Structures of Ca doped sample and annealed Fe 3% sample are rhombohedral while the others are monoclinic(Table.1). Influence of Fe ratio on structure is very small. No other phases or inpurities are observed.

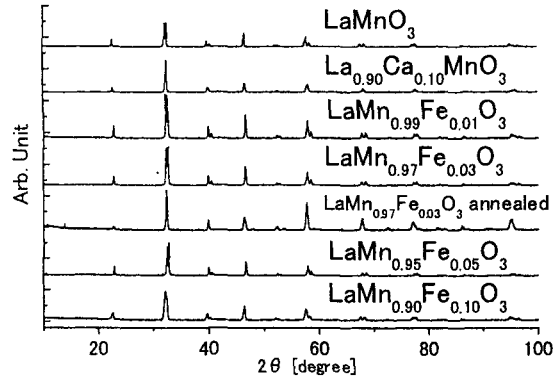

Fig.1 X-ray diffraction patterns of the produced samples.

3.2 VSM measurement

In Fig.2, the temperature dependences of magnetic moment measured by VSM are displayed. All samples are paramagnetic at room temperature and turns ferromagnetic by decreasing temperature. In Fe doped series, Curie temperature and magnetization at low temperature decrease by increasing the Fe ratio. It is also seen that temperature range of magnetic transition broadens. No anti-ferrromagnetic phase is seen in any sample.

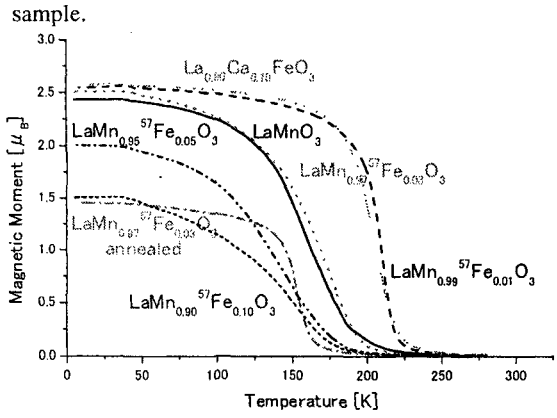

Fig.2 The temperature dependences of magnetic moment of samples. Applied magnetic field is 0.1 T.

3.3 Electric resistivity

In Fig.3, the temperature dependence of resistivity and magnitude of GMR at 5T(($\rho_0 - \rho_{5.0}$)/ ρ_0[%]) for the samples are shown. GMR effect is observed for all the samples. In the Ca doped sample, resistivity and GMR effect become maximum around Curie temperature as is reported in previous studies. When decreasing temperature, resistivity increases until the Curie temperature is reached, and then it decreases under the Curie temperature. This phenomenon indicates the Metal-Insulator transition.

Table 1 Result of X-ray diffraction and VSM measurement. M anf R denote the monoclinic and the rhombohedral crystalline structure, respectively. M_{max} is the maximum value of magnetization obtained from the M-H curves at the lowest temperature.

	Crystal Structure	Tc [K] (at 0.1T)	$M_{max}[\mu_B]$ (at 5T)
$LaMnO_3$	M	190	3.69
$(La_{0.90}Ca_{0.10})MnO_3$	R	220	3.78
$La(Mn_{0.99}Fe_{0.01})O_3$	M	220	3.67
$La(Mn_{0.97}Fe_{0.03})O_3$	M	195	3.44
$La(Mn_{0.95}Fe_{0.05})O_3$	M	180	2.98
$La(Mn_{0.90}Fe_{0.10})O_3$	M	180	2.59
$La(Mn_{0.97}Fe_{0.03})O_3$ annealed	R	160	3.67

$LaMnO_3$ and Fe doped samples also show GMR effect, but they take maxima at temperatures far below the Curie temperature. Resistivity exponentially increases as temperature decreases. Metal-Insulator transition does not exist. As Fe ratio increases, resistivity increases at low temperature.

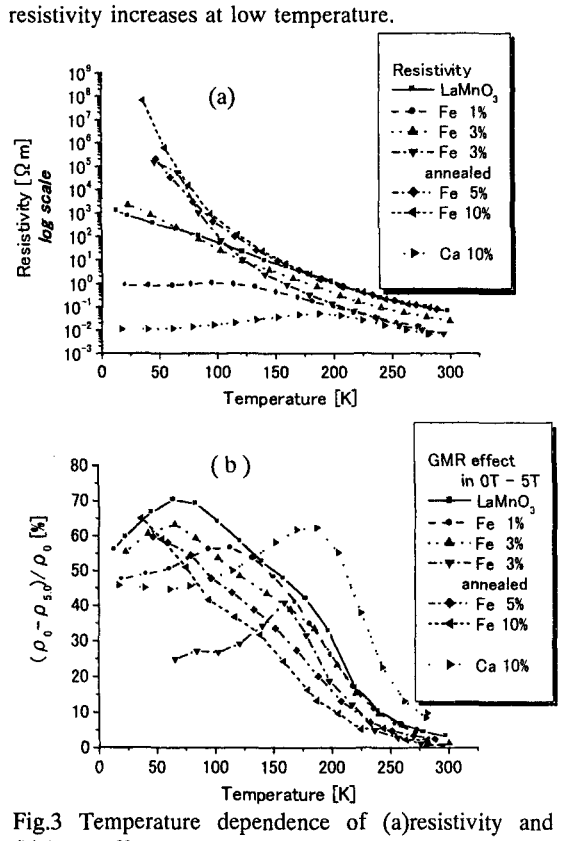

Fig.3 Temperature dependence of (a)resistivity and (b)GMR effect.

3.4 Mössbauer spectroscopy

Mössbauer spectra of the annealed Fe3% doped sample measured at various temperatures are shown in Fig.4. Spectra consist of 2 ferromagnetic sextets and 1 paramagnetic doublet at low temperature, while only 1

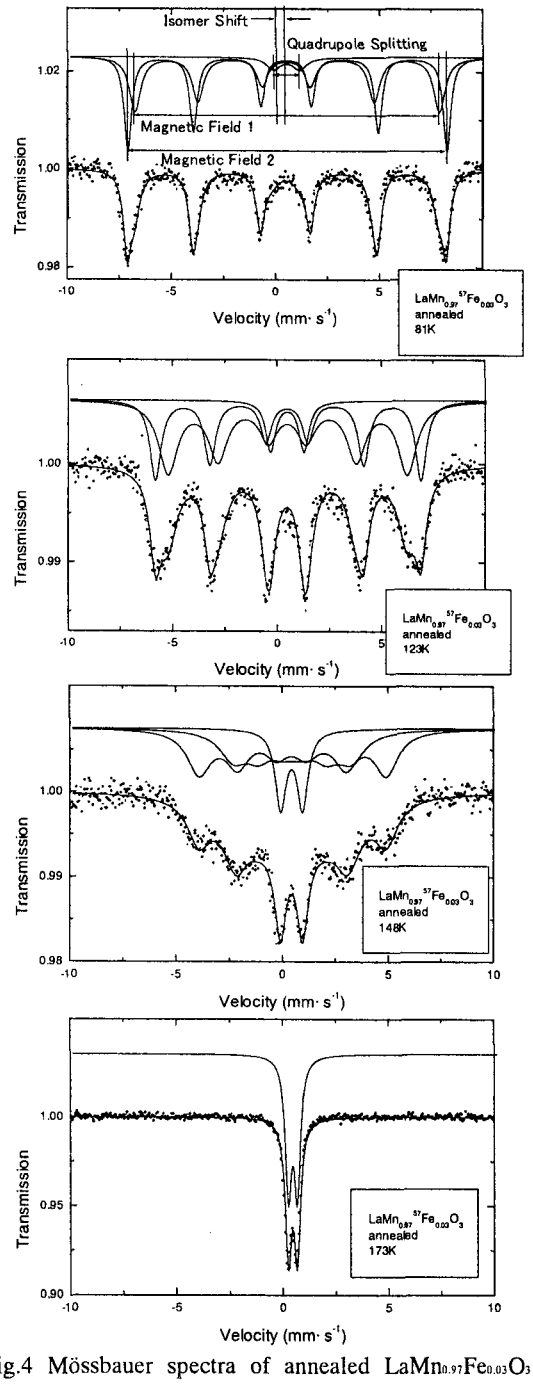

Fig.4 Mössbauer spectra of annealed $LaMn_{0.97}Fe_{0.03}O_3$ sample.

doublet is observed at high temperature. The existence of 2 sextets means that there exist 2 ferromagnetic sites with different internal fields. The ratio of sites and magnitude of internal magnetic fields decrease as temperature decreases.

Fitting parameters of the observed Mössbauer spectra are shown in Fig.5. From the isomer shift that indicates chemical state of ions, Fe substitutes Mn as Fe^{3+}. This result agrees with the result of ESCA measurement. The line widths at the sextets, which represent how scattered the environment of the magnetic Mn site, increases as temperature increases.

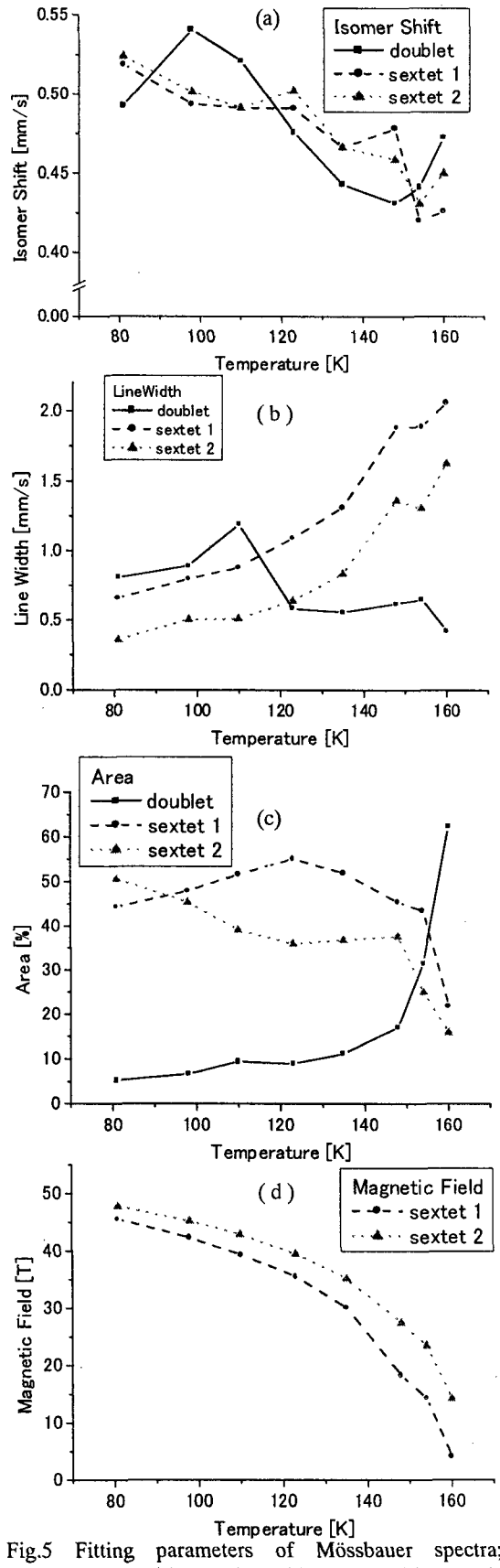

Fig.5 Fitting parameters of Mössbauer spectra; (a)isomer shift, (b)line width, (c)area, and (d)magnetic field.

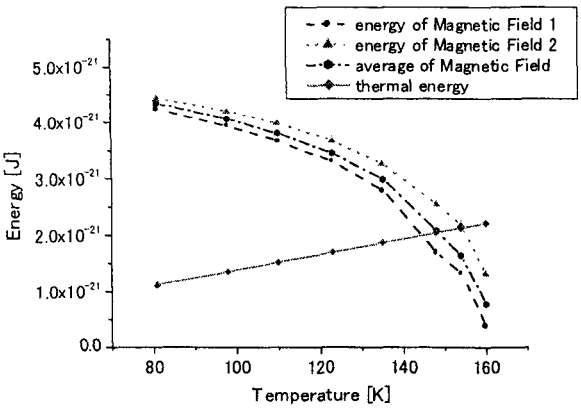

Fig.6 Thermal energy and magnetic energy calculated from fitting parameters of Mössbauer spectra.

The area and magnetic field, which means ratio of sites and internal magnetic field respectively, dissappear around the Curie temperature.

Magnetic energy of Mn site calculated from the area, internal magnetic field and magnetic moment becomes smaller than thermal energy near the Curie temperature as is shown in Fig.6. It can be seen on Fig.3(b) that GMR effect becomes maximum around this temperature.

4. DISCUSSION

Crystalline structure of Fe doped samples which are not annealed are monoclinic, where those for the Ca doped sample and the annealed Fe 3% sample are rhombohedral. This difference is presumed to be due to the difference of ion size and deoxidization.

Though all samples are ferromagnetic at low temperature, they show GMR effect. In previous studies, it is said that GMR effect originates from antiferromagnetic spin arrangement of the moments on the Mn site. We think that our samples must have antiferromagnetic arrangement too, but we don't think that macroscopic ferromagnetic property is necessary.

It is said that crystalline structures play an important role for GMR effect, and large GMR effect are observed at samples with a rhombohedral strcture. However, in the present case, GMR effects are observed in Fe doped samples with a monoclinic structure. The monoclinic structures of our samples are close to cubic or rhombohedral, so the Mn-O-Mn angle was adequate for hole transfer and double exchange interaction.

For the Fe doped samples, no metal-insulator transition is observed. GMR effect in La-Mn oxides have been related to magnetic transition and metal-insulator transition, but from our observation, it is appropriate to think that metal-insulator transition is not necessary for the GMR effect in our system and magnetic transition is essential.

Mössbauer spectra showed that magnetic moment dissappeared when magnetic energy becomes smaller than the thermal energy. This means that arrangement of magnetic moment is weakened by thermal energy, so spin of electron easily rearranged to ferromagnetic arrangement by external magnetic field, and GMR effect takes a maximun at this temperature.

From these results, we conclude that Fe doped samples were neither antiferromagnetic nor ferromagnetic but cant-ferromagnetic. Cant-ferromagnetic spin arrangement means that directions of the spins are almost the same, but slightly canting. Thus the property of sample is antiferromagnetic microscopically, ferromagnetic macroscopically. When external magnetic field is supplied, spins become completely ferromagnetic. This mechanism is not certified theoretically yet, but it can explain our observation well.

5. CONCLUSION

GMR effect in $LaMnO_3$ and $LaMn_{1-x}Fe_xO_3$ samples are observed. GMR effect increases when resistivity increases, but the temperature at which GMR effect becomes maximum is far from the Curie temperature except for annealed $LaMn_{0.97}Fe_{0.03}O_3$ and $La_{0.90}Ca_{0.10}MnO_3$. The samples are not antiferromagnetic but ferromagnetic at low temperature. No Metal-Insulator transition is observed in $LaMnO_3$ and $LaMn_{1-x}Fe_xO_3$ samples.

From the Mössbauer spectra, the temperature at which magnetic energy became smaller than thermal energy agreed with the temperature GMR effect takes a maximum. From these results, we conclude that the GMR effect in the Fe doped samples originates from the cant-ferromagnetism of the Mn sites.

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