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Electromagnetic and structural properties in $(La,Y)(Mn,Ni)O_{3+\delta}$

Akio Yamamoto and Katsuro Oda
Institute of Industrial Science, University of Tokyo, 4-6-1 Komaba, Meguro-ku, Tokyo 153-8505, Japan
Fax: 81-3-5452-6326, e-mail: akio@iis.u-tokyo.ac.jp

Perovskite manganites are known to show negative colossal magnetoresistance (CMR) effect. Since the partial replacement of Mn^{3+} by Ni^{2+} causes the conversion of Mn^{3+} to Mn^{4+}, there exists CMR in $La(Mn,Ni)O_3$. Furthermore, the excess oxygen also introduces the mixed valence of Mn ions in these specimens. On the other hand, the crystallographic symmetry is hexagonal in the Ni slightly doped specimen. When the symmetry approaches cubic, the Curie temperature is expected to increase by double exchange interaction. The partial replacement of La^{3+} by Y^{3+} causes the structural change, and magnetic and transport properties change. So, We investigated electromagnetic and structural properties in $(La,Y)(Mn,Ni)O_{3+\delta}$. The Ni doped specimens do not show metal-insulator transition. The Y doped specimens in $La(Mn,Ni)O_{3+\delta}$ show higher structural symmetry at room temperature. As the structural symmetry grows, magnetization at low temperature increases but CMR effect is suppressed.
Key words: magnetoresistance, manganite, structural symmetry, magnetic transition

1. INTRODUCTION

Perovskite manganites $(La_{1-x}A_x)MnO_3$ (A=Ca,Sr, etc.) are known to show negative colossal magnetoresistance (CMR) effect [1-5]. The partial replacement of La^{3+} by A^{2+} ions causes the conversion of Mn^{3+} to Mn^{4+}, and the magnetic and transport properties of the manganites change. The mixed valence of Mn ions leads to strong ferromagnetic (FM) interaction arising from the Mn^{3+}-O-Mn^{4+} bonds. In general, it is considered that this FM interaction originates from the double exchange (DE) mechanism proposed by Zener [6]. According to the DE mechanism, charge carriers become itinerant among the FM interaction zones. The switching to the FM configuration is then facilitated by an applied field, and the percolative pathways between conductive parts are responsible for the observed large resistivity decrease. Fäth et al. investigated single crystals and thin films of $(La_{1-x}Ca_x)MnO_3$ by using scanning tunneling spectroscopy. They showed that below T_c a phase separation (PS) is observed where inhomogeneous structures of metallic and more insulating areas coexist and are strongly field dependent in their size and structure [7]. Uehara et al. showed that in $(La_{5/8-y}Pr_yCa_{3/8})MnO_3$ with y ~ 0.35, giant clusters of FM and charge ordered (CO) phases coexist at low temperature [8]. Furthermore, Moreo et al. reported the generation of large coexisting metallic and insulating clusters in doped manganites by computational studies [9,10].

The competition between FM and antiferromagnetic (AFM) interactions in manganites causes magnetic frustration like spin glass or cluster glass [11,12]. In $La(Mn_{0.9}Ni_{0.1})O_{3+\delta}$, it is found that structural symmetry is lower in the temperature region where magnetic frustration takes place than that in other FM temperature region [13]. It is suggested that the extent of magnetic frustration which originates from the structural change increases or decreases the conductive pathways among FM regions below T_c in this specimen. It is found that MR increases in the low temperature where magnetic frustration takes place in $La(Mn_{0.9}Ni_{0.1})O_{3+\delta}$ [13].

It is well known that 3d magnetic metal ions form stable perovskite oxides together with rare-earth atoms which show various magnetic and transport behaviours. Mn^{3+} ions are ions which induce Jahn-Teller distortion, and the ionic radius of Ni^{2+} is larger than that of Mn^{3+}. On the other hand, a theory of the role of covalence in the perovskite-type manganites was reported by Goodenough [14]. This theory indicates that the magnetic exchange interaction between Ni ions and Mn ions separated by an anion O^{2-} can be expected to be ferromagnetic. Ionic radii of La^{3+} and Y^{3+} are 1.22 and 1.04 Å, respectively [15]. The substitution of La^{3+} by Y^{3+} in $La(Mn_{0.9}Ni_{0.1})O_{3+\delta}$ results in structural change.

In the temperature region where structural symmetry is high below T_c, magnetic frustration is small due to FM interaction stabilized by DE mechanism in $La(Mn_{0.9}Ni_{0.1})O_{3+\delta}$ [13]. It is expected from this point of view that T_c increases due to DE mechanism when the structural symmetry is high. It is suggested that structural change causes magnetic change for ferromagnetic interactions introduced by DE mechanism between Mn ions and superexchange (SE) mechanism between Ni^{2+} ion and Mn ion. In this paper, this relation between T_c and structural change that takes place by partial replacement of La^{3+} by Y^{3+} in $La(Mn_{0.9}Ni_{0.1})O_{3+\delta}$ is investigated.

2. EXPERIMENTAL

We prepared specimens with the compositions of $(La_{1-y}Y_y)(Mn_{0.9}Ni_{0.1})O_{3+\delta}$ (y=0, 0.04) by conventional solid state reaction method in oxygen atmosphere. The proper ratio of La_2O_3, Y_2O_3, MnO_2 and NiO was mixed and calcined at 1223K for 12 hours. And then, the powders were ground for 2 hours, pressed into pellets, and sintered at 1473K. The two types Y 4 % doped specimens were sintered for the following hours. The

one sintered at 1473K for 18 hours is named specimen (b). This sintering temperature and time is the same for $La(Mn_{0.9}Ni_{0.1})O_{3+\delta}$ which is named specimen (a). The other Y doped specimen (c) was prepared by sintering three times at 1473K for 18 hours.

The phases of prepared specimens were identified by X-ray powder diffraction method. The precise lattice parameter was measured by mixing the specimen with Si powder. The MR measurements were performed with and without applying external magnetic field with the temperature interval of 20K between 300K and low temperature. Temperature dependence of magnetization (MT curves) was measured by vibrating sample magnetometer (VSM) produced by Toei Industry. The Curie temperature (T_c) was determined from the maximum point obtained from $|dM_{ZFC}/dT|$. We measured MT curves after cooling the specimen from 290K to 30K in zero field (ZFC).

3. RESULTS AND DISCUSSION

3.1 X-ray measurement

All of the specimens are confirmed to be perovskite type. The symmetry is hexagonal. For the X-ray patterns, see the preceding paper [16]. Figure 1 shows the maximum peak of diffraction patterns in specimens. When c/a approaches 2.45, the structural symmetry becomes higher. Here, c/a is ratio of lattice parameter when the hexagonal basis is applied. The values of c/a for specimen (a), (b) and (c) are 2.420, 2.431 and 2.439 at room temperature, respectively. Both of the Y doped specimens (b) and (c) indicate higher structural symmetry than the only Ni doped specimen (a) at this temperature.

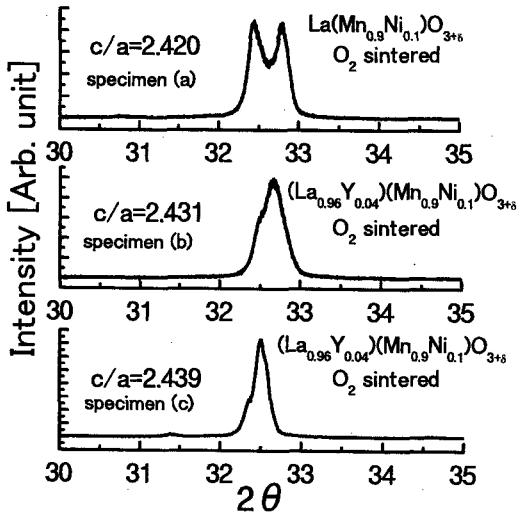

Figure 1 The diffraction patterns near the maximum peak of specimens.

3.2 Magnetization

Figure 2 shows the temperature dependence of magnetization measured during the warming process with a applying a field of 70 Oe after zero field cooled (M_{ZFC}). All of the specimens are ferromagnetic at low temperature. The values of T_c for specimen (a), (b) and (c) are 94K, 111K and 144K, respectively. T_c of the specimen (a) is lower than Ni 10% doped specimen which is sintered in air [16,17]. This is because the specimen (a) sintered in oxygen atmosphere has more amount of excess oxygen than the other specimen sintered in air [17].

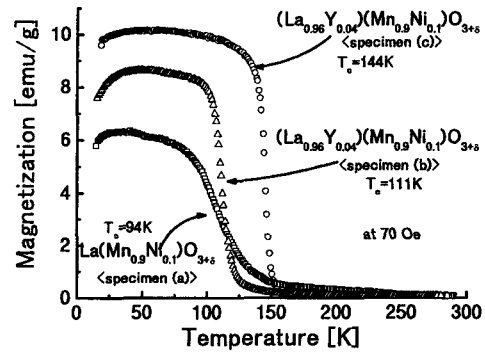

Figure 2 The temperature dependence of magnetization after cooling the specimen (M_{ZFC}).

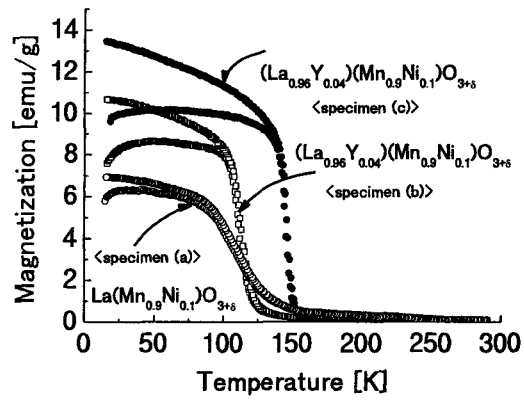

Figure 3 The temperature dependence of M_{FC} and M_{ZFC}

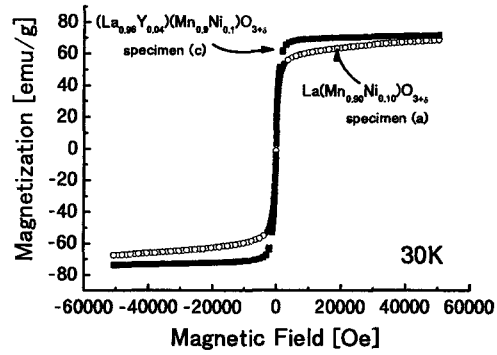

Figure 4 The magnetic field dependence of magnetization at 30K

Figure 3 shows M_{ZFC} and M_{FC}. Here, M_{FC} is measured with applying a field of 70 Oe from room temperature to low temperature. The difference between M_{ZFC} and M_{FC} could be due to the magnetic frustration introduced by AFM and FM interactions [11,12]. We reported that the irreversibility indicates the existence of a cluster glass in $La(Mn_{0.9}Ni_{0.1})O_{3+\delta}$

[16]. The cluster glass is characterized by the large deviation between M_{ZFC} and M_{FC} at low temperature and gradual reduction of M_{ZFC} when decreasing the temperature [11,12]. As can be seen from figure 3, in all of the specimens, it can also be presumed that the competition between the clusters of the FM and the AFM regions introduce such a complex magnetic frustration.

Figure 4 shows the magnetic field dependence of Magnetization at 30K. Both of the specimen (a) and (c) are ferromagnetic at this temperature. Magnetization of 5T is 2.97 and 3.07 μ_B in specimen (a) and (c), respectively. Assuming that Mn^{4+}, Mn^{3+} and Ni^{2+} takes a FM alignment and there is no excess oxygen in specimens, the calculated effective Bohr magnetron of specimen (a) and (c) is 3.7 μ_B. Here, the effective Bohr magnetron of Mn^{3+}, Mn^{4+} and Ni^{2+} ions used are 4, 3 and 2 μ_B, respectively. This difference between magnetization with a field of 5T and this calculation indicates that Mn^{4+} is introduced not only by Ni^{2+} but also by excess oxygen and that these specimens contain AFM alignments of the SE interaction between Mn^{3+} ions etc.. The competition between FM and AFM like this causes magnetic frustration with a weak field which is seen in figure 3.

3.3 Resistivity and MR

Figure 5 shows the temperature dependence of resistivity. All of the specimens do not exhibit metal-insulator transition in the temperature region where measurements were taken out. The resistivity of these specimens increases monotonically when the temperature decreases. It is found that the resistivity of the Y doped specimens increases slower than specimen (a) when decreasing temperature.

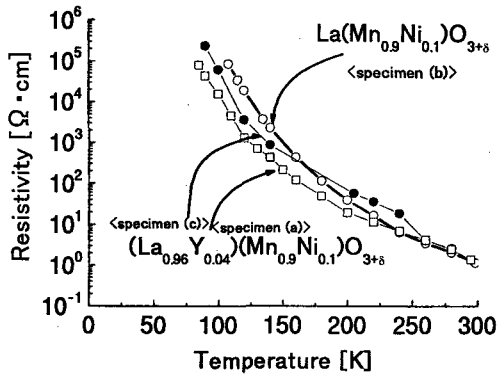

Figure 5 The temperature dependence of resistivity

Figure 6 shows the temperature dependence of MR effect. The magnitude of MR is estimated by the value, $MR = (\rho_{0T} - \rho_{5T})/\rho_{0T}$, where ρ_{0T} and ρ_{5T} are the resistivities without a magnetic field and with a field of 5T, respectively. The CMR effect near T_c is 56%, 46% and 28% for the specimen (a), (b) and (c), respectively. It is found that CMR effect is smaller in specimen (b), (c) than specimen (a). It is also found that the temperature dependence of MR in specimen (c) is small between 200K and 150K in comparison with other temperature regions. On the other hand, specimen (b) with the same Y amount does not show the temperature dependence of MR like this.

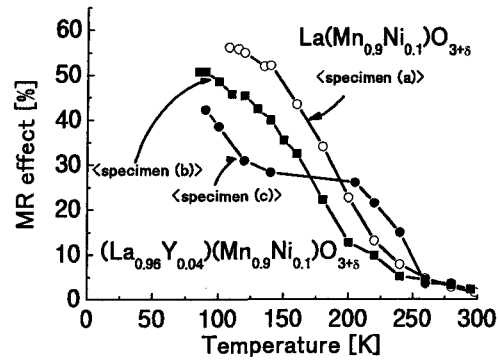

Figure 6 The temperature dependence of MR

3.4 The relation among the Curie temperature, structural symmetry and MR

All of the specimens indicate ferromagnetism from figure 2,3,4. This is mainly because DE mechanism between Mn^{3+} and Mn^{4+} introduced by excess oxygen and the Ni substitution. On the other hand, it is also known that ferromagnetic interaction of SE mechanism between Ni^{2+} and $Mn^{3+/4+}$ [14]. It is found that magnetization and T_c is larger when the structural symmetry is higher at room temperature. When decreasing temperature, the resistivity of Y doped specimens with high structural symmetry increases slower in comparison with specimen (a). These results mean that ferromagnetic interaction by moving holes explained by DE mechanism are stronger in specimen (b) and (c) than in specimen (a). CMR effect of Y doped specimen with high structural symmetry decreases. This result shows that CMR of the specimen with high structural symmetry decrease due to DE mechanism.

MR is connected with the ratio of the spin direction when the magnetic field is applied or not. When this ratio is large, MR increases. On the other hand, the coexistence of FM and AFM phases in manganites was reported on previous papers [8]. It was also reported that in $La(Mn_{0.9}Ni_{0.1})O_{3+\delta}$ MR is related by the extent of the FM region whether or not a constant field is applied [15]. It is suggested that the different ratio of FM and AFM region between specimen (b) and (c) sensitively causes the difference of the temperature dependence of MR.

5. IN SUMMARY

Three type specimens were prepared by partial replacement of La by Y or with different sintered time. All of the specimens indicate ferromagnetism and magnetic frustration at the low temperature. When the structural symmetry is high at room temperature, the Curie temperature increases because carriers move smoothly at low temperature due to double exchange mechanism. It is expected that further increase of T_c and MR is possible by control of the structural symmetry.

6. ACKNOWLEDGMENTS

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