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THE RELATION OF THE MAGNETORESISTANCE AND MAGNETIC FRUSTRATION AMONG FERROMAGNETIC CLUSTERS IN $La(Mn_{1-x}Ni_x)O_{3+\delta}$

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Abstract. Colossal magnetoresistance (CMR) properties of $La(Mn_{1-x}Ni_x)O_{3+\delta}$ ($0 \leq x \leq 0.1$) are investigated. The partial replacement of Mn^{3+} by Ni^{2+} causes the conversion of Mn^{3+} to Mn^{4+}. However, the CMR effect of the manganites with excess oxygen decreases as the Ni amount is increased. The samples were prepared both in air and in oxygen atmosphere in order to change the Mn^{4+} ratio and the concentration of Mn^{4+} was determined quantitatively. We measured the temperature dependence of magnetization after cooling the sample in zero field (ZFC) or in the field (FC). According to the temperature dependence of coercive field and thermoremanent magnetization, a cluster glass like transition is presumed. We propose that the frustration of the interaction among ferromagnetic clusters introduced by substituting Ni for Mn causes the decrease and increase of the magnetoresistance.

1. INTRODUCTION

Perovskite manganites $La_{1-x}A_xMnO_3$ (A = Ca,Sr, *etc.*) are known to show negative colossal magnetoresistance (CMR) effects [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 valency of Mn ions leads to strong ferromagnetic (FM) interaction among 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].

It is well known that 3d magnetic metal ions together with rare earth ions form stable perovskite oxides that show various magnetic and transport behaviors. Furthermore, Mn^{3+} ions are Jahn-Teller ions, and the radius of Ni^{2+} ions is still larger than that of Mn^{3+}. Therefore, by substituting Mn^{3+} ions with Ni^{2+} ions, we expect further strain to be induced. Asai *et al.* proposed that nickel is in the divalent state, and that Ni^{2+} and Mn^{4+} align ferromagnetically, also based on the superexchange (SE) interaction between Ni^{2+} and Mn^{4+} [7]. Hébert *et al.* also indicated from the investigation for $LaMn_{1-x}Ni_xO_3$ ($x \leq 0.2$) that nickel behaves like a divalent cation [8]. The theory of the role of covalence in the perovskite-type manganites has been reported by Goodenough [9]. According to his theory, Mn^{3+} and Ni^{2+}, or Mn^{4+} and Ni^{2+}, align ferromagnetically. It would be interesting to study the charge mobility, magnetoresistance (MR) and magnetization from the point of view of the magnetic exchange interaction within the Mn-O-Mn network when the partial replacement of Mn^{3+} by Ni^{2+} ions causes the conversion of Mn^{3+} to Mn^{4+}.

We previously reported that the Ni 10% doped specimen shows cluster glass behavior from the temperature dependence of dc magnetization, ac susceptibility in the field cooled (FC) and zero field cooled (ZFC) conditions [10,11]. We suggested that the temperature dependence of the MR effect in $LaMn_{1-x}Ni_xO_{3+\delta}$ ($0 \leq x \leq 0.1$) is related to the spin frustration with charge localization at lower temperature that is caused by the Ni^{2+} doped into Mn sites [11].

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So, in this paper, we investigate the temperature dependence of coercive field that reduce the thermoremanent magnetization to zero in Ni 10% doped specimens. We report the relation between the MR effect and the magnetic frustration among ferromagnetic clusters.

2. EXPERIMENTAL

In order to investigate MR and magnetic properties of Ni doped manganites, we prepared specimens with the compositions of $LaMn_{1-x}Ni_xO_{3+\delta}$ (x=0.1) by conventional solid state reaction method. In order to change the oxygen concentration, two specimens were prepared. One was annealed in air, and the other was in oxygen. The proper ratio of MnO_2, NiO, and La_2O_3 was mentioned elsewhere [10,11]. These powders were mixed with proper ratio for more than 2 hours and calcined in air at 1223K for 12 hours in air or oxygen atmosphere. And then, the powders were ground for 2 hours, pressed into pellets, sintered in air or oxygen atmosphere at 1473K for 18 hours. Here, these two $LaMn_{0.9}Ni_{0.1}O_{3+\delta}$ specimens which are prepared in air and in oxygen atmosphere are named specimen (a) and specimen (b), respectively.

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. The interval of the magnetic field was 0.5T between +5T to -5T. Resistivity was measured by four probe method, and the current direction was paralled to magnetic field. The amount of Mn^{4+} was determined by iodometric titrations using sodium thiosulfate. Temperature dependence of magnetization (MT curves) and magnetic field dependence (MH curves) at several temperatures were 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) or in the field of 7 mT (70 Oe) (FC).

3. RESULTS

Both of specimens (a) and (b) are confirmed to be perovskite type. The symmetry is hexagonal. For the X-ray diffraction patterns, see the preceding paper [10]. We have reported that Ni ions exist as Ni^{2+} in

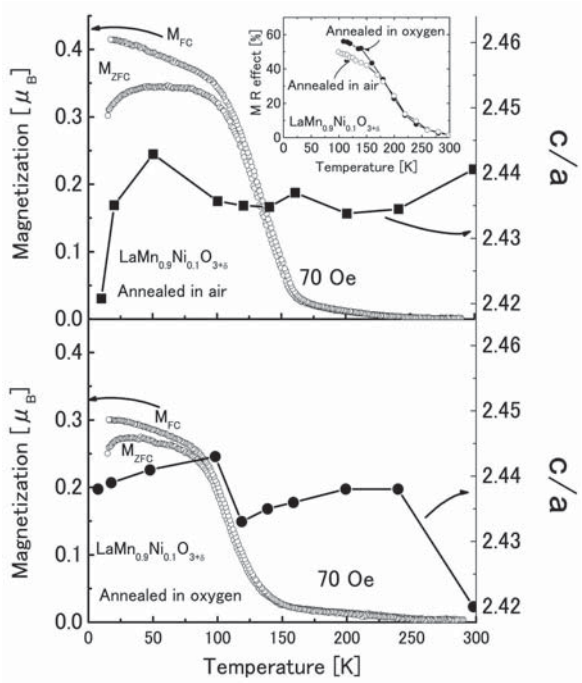

Fig.1. The temperature dependence of M_{ZFC}, M_{FC} and *c/a* in $LaMn_{1-x}Ni_xO_{3+\delta}$ annealed in air (upper graph) or oxygen atmosphere (lower graph). The inset (upper graph) is the temperature dependence of MR effect.

$LaMn_{0.9}Ni_{0.1}O_{3+\delta}$ [10]. Therefore, from the results of ICP and iodometric titrations, Mn^{4+}/(Mn+Ni) of specimen (a) is derived to be 29.2±1.4%. The ratio for specimen (b) is 43.0±1.5%. The amount of excess oxygen, δ, is 0.047±0.030 and 0.135±0.032 for specimen (a) and (b), respectively.

Fig. 1 shows the temperature dependence of *c/a*, M_{ZFC} and M_{FC}. Here, *c/a* is the ratio of lattice parameter in a warming process at zero field. Here, the hexagonal basis is applied. When *c/a* is equal to 2.45, the structural symmetry is cubic. As *c/a* deviates from 2.45, distortion is introduced. The ZFC and FC process are mentioned elsewhere [11]. It is found that a deviation exists between M_{ZFC} and M_{FC} at low temperature. T_C is 146K and 106K for specimen (a) and (b), respectively. It can be seen from these results that c/a is smaller at the temperature region near T_C than at the temperature region where M_{ZFC} is high.

Both of specimens (a) and (b) do not exhibit metal-insulator transition in the temperature region where measurements were carried out. The resis-

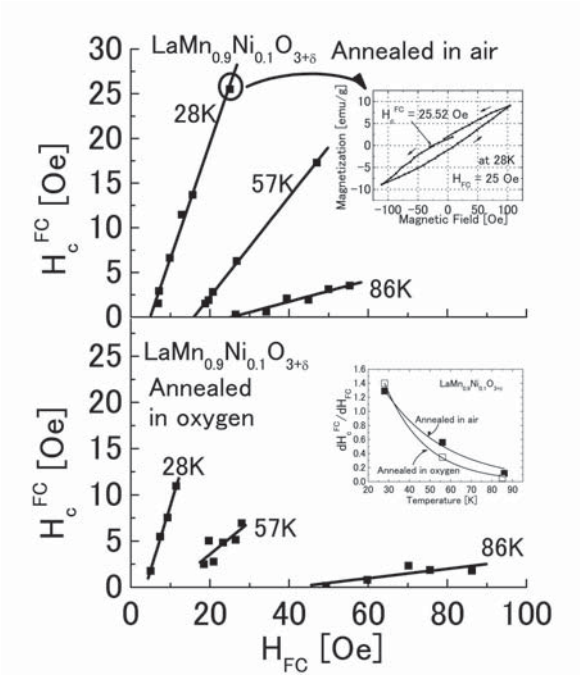

Fig. 2. Plot of the cooling field (H_{FC}) vs the field cooled coercivity (H_c^{FC}) at the corresponding cooling field at different temperatures in $LaMn_{1-x}Ni_xO_{3+\delta}$ annealed in air (upper graph) or oxygen atmosphere (lower graph). The solid lines show the linear fit. The inset of upper graph is the hysteresis loop drawn under 25 Oe at 28K. The inset of lower graph is plot of dH_c^{FC}/dH_{FC} as a function of temperature. The solid lines show the exponential fit.

tivity of these specimens increases monotonically when the temperature is decreased. The resistivity of specimen (a) is a slightly little in comparison with that of specimen (b) at the temperature where measurements were taken out. The inset on Fig.1 shows the temperature dependence of MR effect in those specimens. (The magnitude of $MR = (\rho_{0T} - \rho_{5T})/\rho_{0T}$, where ρ_{0T} and ρ_{5T} are the resistivities without an external magnetic field and with a field of 5 T, respectively.) The MR effect of the $LaMn_{0.9}Ni_{0.1}O_{3+\delta}$ measured at the temperature around T_C is 43% and 56% for specimens (a) and (b), respectively. In the low temperature region, the MR effect of the former is smaller than that of the latter.

It is known that hysteresis loops drawn under the FC condition show various type of structures for spin glass and cluster glass [12]. Under the FC condition, we cool the specimen down to 20K with a field, which indicates H_{FC}. Then, after the specimen is warmed to different selected temperatures (28K, 57K, 86K) that are below T_C, the field is first reduced to zero and then made to follow the cycle between 0 Oe → -100 Oe → +100 Oe → 0 Oe. The observed hysteresis loop under cooling field 25 Oe is shown in the inset of Fig. 2 (upper graph). By increasesing H_{FC}, the negative field at which the MH curve cuts the H axis increases. This field may be called FC coercivity (H_c^{FC} as marked by the arrow in the inset of Fig.2 (upper graph)). This field reduces the thermoremanent magnetization (TRM) to zero. Fig. 2 shows the plot of the FC coercivity (H_c^{FC}) versus the cooling field (H_{FC}) at the corresponding cooling field. It is found that the relation between H_{FC} and H_c^{FC} is linear at a given temperature. The slope of these curves at different temperatures gives the FC coercivity in the unit field at the corresponding temperature. Therefore, TRM at the different temperature can be estimated from the slope. The inset of Fig. 2 (lower graph) shows the temperature dependence of dH_c^{FC}/dH_{FC}. The dH_c^{FC}/dH_{FC} of specimen (b) is slightly larger at 28K in comparison with that of (a). However, as the temperature increases, the former becomes smaller than the latter.

4. DISCUSSION

The lack of La and Mn sites is caused by the excess oxygen in the specimen. When the amount of the lack for La and Mn is large or the structure is distorted, it is proposed that the charge mobilities introduced by DE interaction with ferromagnetic interaction are small. This is the reason why T_C of specimen (b) is smaller than that of (a).

The difference between M_{ZFC} and M_{FC} could be due to the magnetic frustration introduced by AFM and FM interactions [12,13]. We reported that the irreversibility indicates the existence of a cluster glass in $LaMn_{0.9}Ni_{0.1}O_{3+\delta}$ [11]. As can be seen from Fig.1, in both of specimens (a) and (b), it can also be presumed that the competition between the clusters of the FM and the AFM regions introduce such a complex magnetic frustration. It is found from Fig.1 that the magnetization has a connection with structural symmetry. When *c/a* is close to 2.45, M_{ZFC} becomes large. The reason for this is that the FM phase is more stabilized by DE interaction and the charge carriers' mobilities are high when the structural symmetry is good. Specimen (b) possesses higher amount of Mn^{4+} than specimen (a). This is the reason why MR of the former is larger than that of the latter. In general, it is said that MR effect takes a maximum near T_C due to the DE mechanism However, in these $LaMn_{0.9}Ni_{0.1}O_{3+\delta}$ specimens, distortion is introduced at around T_C, since *c/a* de-

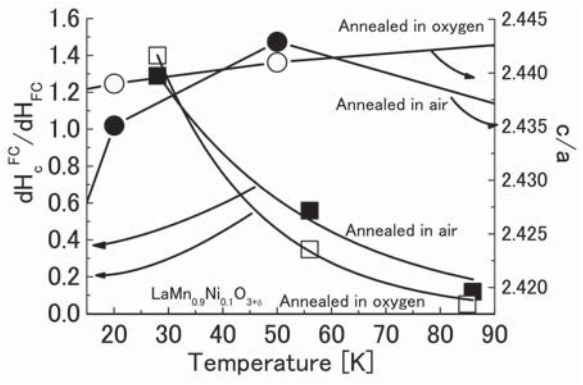

Fig.3. The temperature dependence of dH_c^{FC}/dH_{FC} and *c/a*.

viates more from 2.45 with the change of M_{ZFC}. We propose that the big MR effect is caused not only by DE interaction but also from some structural change with the change of the magnetization. Concerning the decrease of the CMR effect when the Ni amount is increased, see the preceding paper [10].

Mukherjee *et al.* reported that in $La_{0.5}Sr_{0.5}CoO_3$, a characterization of cluster glass has been observed, and the temperature dependence of dH_c^{FC}/dH_{FC} was proportional to $\exp(-\alpha T)$ with α=0.01 [12]. This exponential temperature dependence of H_c^{FC} indicates that the blocking of these clusters decreases exponentially when the temperature increases the disorder of spin arrangements due to thermal activation. Since the temperature dependence of magnetization for $LaMn_{0.9}Ni_{0.1}O_{3+\delta}$ also shows the characteristic of cluster glass, we also fit the temperature dependence of dH_c^{FC}/dH_{FC} with $A\exp(-\alpha T)$. The results of the fits are good in both of the specimens as can be seen in the inset of Fig.2 (lower graph). The values derived for α are 0.03 and 0.05 for specimen (a) and (b), respectively. It can be seen that the blocking of ferromagnetic clusters is strong against increasing temperature when α is small. The reason why α of specimen (a) is smaller than that of (b) is because the former has a smaller amount of excess oxygen than that of the latter. When applying magnetic field, it aligns the spin direction at the temperature near T_C against thermal energy. We propose that CMR effect is large near T_C when α is large in manganites with a characteristic of cluster glass.

Fig. 3 shows the temperature dependence of dH_c^{FC}/dH_{FC} (TRM) and *c/a*. It is found that TRM remains high when the structural symmetry is high. The reason is because the FM phase is stabilized by DE interaction. We have reported that in ferromagnetic temperature region MR effect was large when *c/a* deviates from 2.45 in the other $LaMn_{0.9}Ni_{0.1}O_{3+\delta}$ specimen [11]. MR effect is strongly related to the difference between the extent of the FM region whether or not a constant field is applied. It is proposed that in the ferromagnetic temperature region, MR effect is large when TRM is small because of the lower structural symmetry.

5. SUMMARY

We prepared specimens with the compositions of $LaMn_{1-x}Ni_xO_{3+\delta}$ (x=0.1) by conventional solid state reaction method in air or oxygen atmosphere. We measured the temperature dependence of magnetization after cooling the sample in zero field (ZFC) or in the field (FC). According to the temperature dependence of coercive field and thermoremanent magnetization, a cluster glass like transition is presumed. We propose that the difference between M_{ZFC} and M_{FC} causes the frustration between FM clusters and AFM regions. We suggest that the temperature dependence of MR effect has a connection with the temperature dependence of M_{ZFC} and structural symmetry in Ni doped specimens. It is found that TRM is large due to DE interaction, when *c/a* is close to 2.45.

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