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Influence of Grain Boundary on Magnetoresistance in $La_{0.7}Ca_{0.3}MnO_3$

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Magnetoresistance (defined in the study as $\Delta\rho(T,H)/\rho(T,0) = (\rho(T,H) - \rho(T,0))/\rho(T,0)$, where $\rho(T,H)$ and $\rho(T,0)$ denote the resistivity at a temperature with and without a magnetic field, respectively) of single and polycrystalline perovskite manganites, $La_{0.7}Ca_{0.3}MnO_3$, and layered perovskite manganites, $La_{1.36}Sr_{1.64}Mn_2O_7$, have been studied to know the influence of grain boundaries. The magnetoresistance of single crystal $La_{0.7}Ca_{0.3}MnO_3$ is almost independent of magnetic field at low temperatures, and the behavior of magnetoresistance is well explained by the model of Searle and Wang which is based on a double-exchange interaction. The magnetoresistance of polycrystalline $La_{0.7}Ca_{0.3}MnO_3$ and $La_{1.36}Sr_{1.64}Mn_2O_7$, decrease drastically for the initial increment of magnetic field ($H \leq 200$kA/m). When a magnetic field is higher than 200kA/m, the values of magnetoresistance decrease gradually with increasing magnetic field. The behavior of magnetoresistance of polycrystalline manganites is quite similar to the studies reported previously and cannot be explained by a model of Raychaudhuri *et al.* which is derived by considering the tunneling of e_g electron through grain boundaries. Moreover, we found that the resistivity of these polycrystalline manganites show the time-dependent nature. These results suggest that we should reconsider the mechanism of the magnetoresistance of polycrystalline perovskite manganites.

Key words: magnetoresistance, perovskite, polycrystalline, manganite, phase transition, rare earth

1. INTRODUCTION

Perovskite manganites, $R_{1-x}A_xMnO_3$ ($0.2 < x < 0.4$), have been studied for many years, and many interesting phenomena, such as metal-insulator transition and colossal magnetoresistance, were reported so far. These phenomena are mainly explained by double-exchange interaction; magnetic interaction between Mn^{3+} and Mn^{4+} which is caused by the hopping of e_g electrons between the two partially filled *d* shells with strong on-site Hund's coupling[1-4].

Recently, Hwang *el al.*[5] investigated the magneto-resistance (MR) of $La_{2/3}Sr_{1/3}MnO_3$ below Curie temperature T_C, and pointed out that there is similarity between the MR of polycrystalline specimen and that of granular nickel films[6]. Raychaudhuri *et al.*[7] investigated the MR of polycrystalline specimens of $La_{0.7-x}Ho_xSr_{0.3}MnO_3$ (x = 0, 0.15) and proposed a tunneling model to explain the behavior of MR of polycrystalline specimens. However, its propriety and the mechanism of this MR has not been clear until now. In order to make this mechanism clear, we need more information on MR of many compounds. In the present study, we investigate MR of single crystal and polycrystalline $La_{0.7}Ca_{0.3}MnO_3$, and for comparison, we also investigate MR of polycrystalline $La_{1.36}Sr_{1.64}Mn_2O_7$ ($La_{2-2x}Sr_{1+2x}Mn_2O_7$, x=0.32) which shows layered perovskite structure[8].

2. EXPERIMENTAL PROCEDURE

Polycrystalline $La_{0.7}Ca_{0.3}MnO_3$ and $La_{1.36}Sr_{1.64}Mn_2O_7$ were prepared by conventional solid state reaction processing. High purity La_2O_3, $SrCO_3$, $CaCO_3$ and Mn_3O_4 were mixed for the compositions mentioned above and calcined in air at 1273K for 12h. Sintering was carried out in air at 1627K for 48h after intermediate grinding. Polycrystalline specimens were cut from sintered disks and its grain size was about 10μm. Single crystal $La_{0.7}Ca_{0.3}MnO_3$ was prepared by a floating zone method. Powder X-ray diffraction measurements show that both compounds can be indexed by a single phase, and the crystal structures of $La_{0.7}Ca_{0.3}MnO_3$ is pseudo cubic (a = 0.5476nm, b = 0.5486nm, $c/\sqrt{2}$ = 0.5486nm) and that of $La_{1.36}Sr_{1.64}Mn_2O_7$ is tetragonal (a = 0.3866nm, c = 2.038nm). From the results of electrical resistivity and magnetization measurements, single crystal and polycrystalline $La_{0.7}Ca_{0.3}MnO_3$ and polycrystalline $La_{1.36}Sr_{1.64}Mn_2O_7$ show the transition from ferromagnetic metal to paramagnetic insulator at about 250K and 125K, respectively.

3. RESULTS

Magnetoresistance (MR) of single crystal and polycrystalline $La_{0.7}Ca_{0.3}MnO_3$ and polycrystalline $La_{1.36}Sr_{1.64}Mn_2O_7$ were measured by applying magnetic fields of up to 5.6MA/m below each Curie temperature. The results of single crystal and polycrystalline $La_{0.7}Ca_{0.3}MnO_3$ are shown in Fig. 1(a) and (b), respectively, and the results of polycrystalline $La_{1.36}Sr_{1.64}Mn_2O_7$ are shown in Fig.1(c), where MR is defined as $\Delta\rho(T, H)/\rho(T,0) = (\rho(T, H) - \rho(T, 0))/\rho(T, 0)$, where $\rho(T, H)$ denote the resistivity at a temperature, T, with a magnetic field, H.

As can be seen from Fig. 1(a), at lower temperatures (T = 4.2K and 77K), the MR is almost independent of magnetic field, and at higher temperatures (T = 150K and 200K), the MR decreases gradually with increasing temperature.

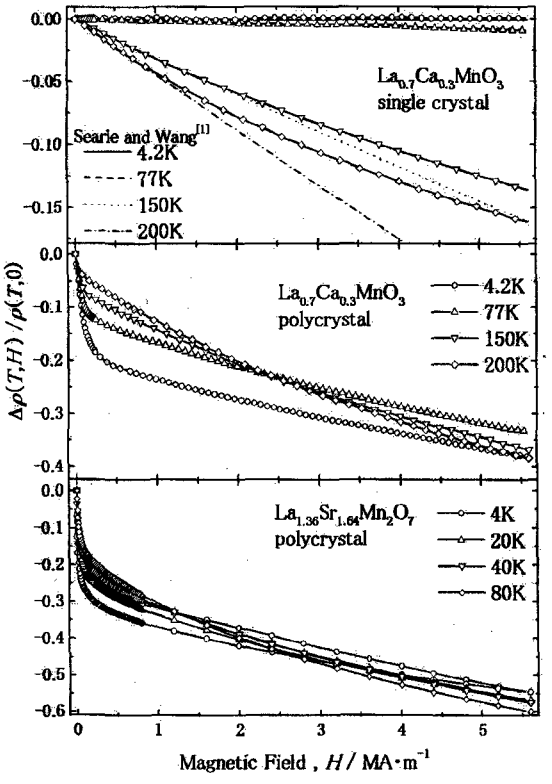

Fig.1 Magnetoresistance as a function of magnetic field up to 5.6MA/m for (a) single crystal $La_{0.7}Ca_{0.3}MnO_3$, (b) polycrystalline $La_{0.7}Ca_{0.3}MnO_3$ and (c) polycrystalline $La_{1.36}Sr_{1.64}Mn2O_7$. The dotted lines in (a) show the calculated magnetoresistances of single crystal $La_{0.7}Ca_{0.3}MnO_3$ by using the model of Searle and Wang

On the other hand, it is noted in Fig.1(b) and (c) that the MR of two polycrystalline specimens are quite different from that of single crystal. That is, the MR of polycrystalline $La_{0.7}Ca_{0.3}MnO_3$ decrease drastically by the initial increment of magnetic field up to 200kA/m and their values at 4.2K are about -0.2, and increase with increasing temperature. When a magnetic field is higher than 200kA/m, the MR decreases gradually with increasing magnetic field up to 5.6MA/m, and its value is about -0.4 at 4.2K. The MR of $La_{1.36}Sr_{1.64}Mn_2O_7$ also decreases drastically field up to 200kA/m and their values at 4.2K are about -0.3. When a magnetic field is higher than 200kA/m, the MR decreases gradually with increasing magnetic field up to 5.6MA/m, and its value is about -0.6 at 4.2K. These behavior of magnetoresistance of both polycrystalline manganites resembles each other, moreover, it is similar to the behavior of the previous studies[5,7].

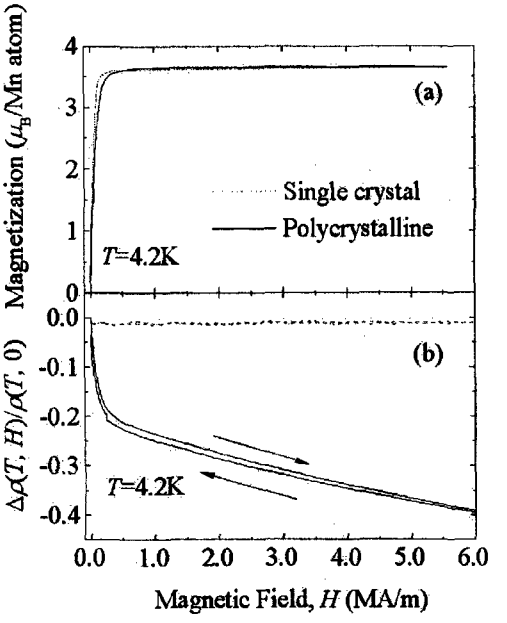

Fig.2 (a) Magnetization curve and (b) magnetoresistance as a function of magnetic field of polycrystalline $La_{0.7}Ca_{0.3}MnO_3$, which are indicated by solid lines, together with those of single crystal $La_{0.7}Ca_{0.3}MnO_3$ for comparison, which are indicated by dotted lines.

To obtain more information on MR of polycrystalline specimens, we measured the magnetization curve of the polycrystalline $La_{0.7}Ca_{0.3}MnO_3$ and compared it with its MR, which is shown in Fig.2. In this figure, magnetization curve and MR of single crystal $La_{0.7}Ca_{0.3}MnO_3$ are also shown for comparison. As can be seen from the figure, the magnetization process is almost the same for polycrystalline and single crystal specimens. However, the MR of polycrystalline specimen is quite different from that of single crystal. That is, the MR of polycrystalline specimen decreases with increasing magnetization, but not for single crystal.

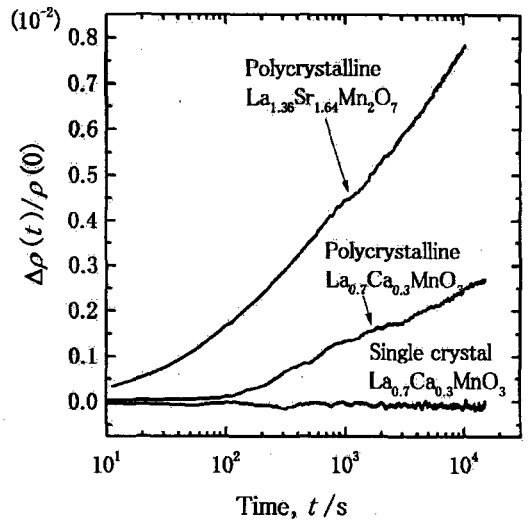

Fig.3 The change of resistivity, $\Delta\rho(t)/\rho(t=0)$ as a function of time for single crystal and polycrystalline $La_{0.7}Ca_{0.3}MnO_3$ and polycrystalline $La_{1.36}Sr_{1.64}Mn_2O_7$, where $\Delta\rho(t)/\rho(t=0)$ is obtained after removing magnetic field from 7.2MA/m to zero.

We also found that the resistivity of these polycrystalline manganites show the time-dependent nature. Then, we measured the resistivity of polycrystalline specimens as a function of time after removing a magnetic field from 7.2MA/m to zero with a sweep rate of 16kA/(m·s). The results of polycrystalline $La_{0.7}Ca_{0.3}MnO_3$ and $La_{1.36}Sr_{1.64}Mn_2O_7$ are shown in Fig.3, where the change of resistivity is defined as $\Delta\rho(t)/\rho(t=0)= (\rho(t)-\rho(t=0))/\rho(t=0)$, where t is the time after removing magnetic field. For comparison, the results of single crystal $La_{0.7}Ca_{0.3}MnO_3$ is also shown. As seen in Fig.3, $\Delta\rho(t)/\rho(t=0)$ of polycrystalline specimens gradually increase as time passes, but not for the single crystal, meaning that time-dependent nature of resistance exists in the polycrystalline specimens, but not in the single crystal specimen. The origin of this time-dependent nature has not been known yet, but it is speculated to be related to the magnetism of the present polycrystalline specimens. For such magnetism, a spin-glass like state can be considered mostly because this magnetism is well known to have time-dependent nature. However, dc-susceptibility of zero field cooling process is almost the same as that of field cooling process, being in good agreement with those of the single crystal. We speculate that a spin-glass like state will appears around the grain boundary only, but not in the grain of the specimen.

4. DISCUSSION

In order to analyze the MR of single crystal and polycrystalline specimens, we will calculate the MR of single crystal and polycrystalline $La_{0.7}Ca_{0.3}MnO_3$ and polycrystalline $La_{1.36}Sr_{1.64}Mn_2O_7$ by using the models previously reported.[7,9]

Searle and Wang[9] proposed a model of resistivity of a single crystal manganite, which is derived based on a double-exchange interaction. According to their model, the electrical resistivity, $\rho(T,H)$, is expressed as,

$$\rho(T,0) = \frac{C}{N}\frac{1-(M(T,H)/M(0,0))^2}{1+(M(T,H)/M(0,0))^2}, \qquad (1)$$

where $M(T,H)$ is the magnetization at a temperature T, and a magnetic field H, N is the density of conductive e_g electrons and C is the constant. Based on eq.(1), we calculated the electrical resistivity of single crystal $La_{0.7}Ca_{0.3}MnO_3$ at zero field (H=0). The calculated results are shown in Fig.4 by open diamonds, together with the experimental ones by a solid line, where temperature is normalized by Curie temperature, T/T_c, and resistivity is normalized by the resistivity at Curie temperature, $\rho(T,0)/\rho(T_C,0)$. As can be seen from the figure, the calculated $\rho(T,0)/\rho(T_C,0)$ are in good agreement with the experimental ones.

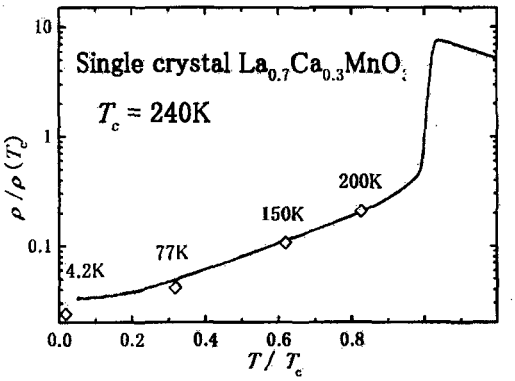

Fig.4 Temperature dependence of experimental (solid line) and calculated (open diamonds) resistivities for single crystal $La_{0.7}Ca_{0.3}MnO_3$, where the calculated values are obtained by using eq.(1).

We also analyze the MR in single crystal $La_{0.7}Ca_{0.3}MnO_3$. By using eq.(1), the MR of $\Delta\rho(T,H)/\rho(T,0)$ is expressed as,

$$\frac{\Delta\rho(T,H)}{\rho(T,0)} = \left(\frac{M(0,0)^2-M(T,H)^2}{M(0,0)^2+M(T,H)^2}\right)\times\left(\frac{M(0,0)^2+M(T,0)^2}{M(0,0)^2-M(T,0)^2}\right)-1, \qquad (2)$$

From eq.(2), we calculated the MR of the single crystal $La_{0.7}Ca_{0.3}MnO_3$, as shown in Fig.1(a) by dotted curves. As seen in this figure, the calculated MR of $\Delta\rho(T,H)/\rho(T,0)$ are in good agreement with experimental ones at magnetic fields lower than 2MA/m. Considering that eq.(2) is adequate at lower magnetic field, we can say that the MR of single crystal specimen is explained

quantitatively by the model by Searle and Wang.[9]

Next, we will analyze the MR of polycrystalline specimens, based on the model derived by Raychaudhuri *et al.*[7] Their model is derived by considering that the MR at low magnetic field ($H \leq 200$kA/m) is due to a tunneling conduction through the grain boundary. According to their model, the electrical conductance, $\sigma(T,H)$, at a temperature T, and a magnetic field H is expressed as,

$$\sigma(T,H) \propto \left(\frac{1}{2}\right)(n_\uparrow + n_\downarrow)^2\left[1+P^2\cos\theta(T,H)\right] = \frac{1}{\rho(T,H)}, \quad (3)$$

where $n_\uparrow$ and $n_\downarrow$ are the density of state of up-spin and down-spin electrons at the Fermi level, respectively; $\theta(T, H)$ is the angle between the magnetic moments of two adjacent grains at a temperature T, and a magnetic field H; and P is the polarization of e_g electron at the Fermi surface, $P=(n_\uparrow - n_\downarrow)/(n_\uparrow + n_\downarrow)$, which is approximately expressed as $M(T, 0)/M(0, 0)$. Using eq.(2), MR of $\Delta\rho(T, H)/\rho(T, 0)$ is expressed as,

$$\frac{\Delta\rho(T,H)}{\rho(T,0)} = \frac{\rho(T,H)-\rho(T,0)}{\rho(T,0)} = \frac{P^2 < \cos\theta(T,0) > -P^2 < \cos\theta(T,H) >}{1+P^2 < \cos\theta(T,H) >}, \quad (4)$$

where $\theta(T, 0)$ is the angle between the magnetic moments of two adjacent grains at zero field and $<\cos\theta(T, H)>$ is an average of $\cos\theta(T, H)$. It should be noted in eq.(4) that when the magnetization is saturated, $<\cos\theta(T, 0)>$ is only unknown parameter because P and $\Delta\rho(T, H)/\rho(T, 0)$ are obtained experimentally and $<\cos\theta(T, H)>$ comes to be 1, considering that the magnetic moments for all the grains are aligned to the magnetic field direction. Then we calculated $<\cos\theta(T, 0)>$ as a function of temperature based on eq.(4). The calculated values $<\cos\theta(T, 0)>$ of polycrystalline $La_{0.7}Ca_{0.3}MnO_3$ and $La_{1.36}Sr_{1.64}Mn_2O_7$ are shown in Fig.5, where $<\cos\theta(T, 0)>$ for both specimens increase with increasing temperature. This temperature dependence of $<\cos\theta(T, 0)>$ contradicts with the fact that $<\cos\theta(T, 0)>$ depends only on the configuration of grain, and therefore it does not depend on temperature. Thus, the MR of polycrystalline manganites investigated in the present study cannot be explained by the above model proposed by Raychaudhuri *et al.*[7]

On the other hand, when a magnetic field is higher than 200kA/m, MR of polycrystalline specimens decreases gradually with increasing magnetic field up to 5.6MA/m, as mentioned before.

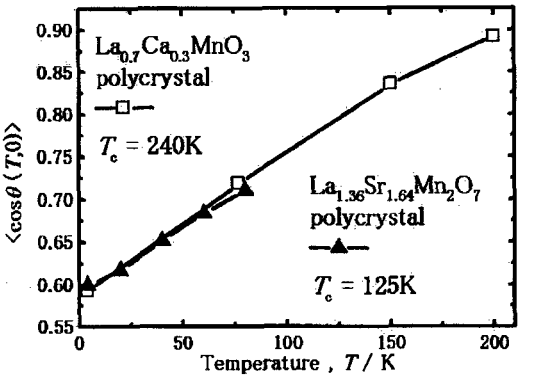

Fig.6 Temperature dependence of $<\cos\theta(T,0)>$ for polycrystalline $La_{0.7}Ca_{0.3}MnO_3$ and $La_{1.36}Sr_{1.64}Mn_2O_7$, which are obtained by using eq.(4).

The decrease is probably caused by the suppression of magnetic fluctuation around grain boundaries because magnetic moments of all grains are already aligned to the direction of magnetic field. However, this behaviour of MR has not been clarified yet. In this way, we should construct a new model which can explain all of the MR behavior of polycrystalline manganites in the present study. This is the future problem.

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