Influence of Grain Boundary on Magnetoresistance in Hole Doped Manganites $\text{La}_{0.7}\text{Ca}_{0.3}\text{MnO}_3$, $\text{La}_{0.7}\text{Sr}_{0.3}\text{MnO}_3$ and $(\text{La}_{0.75}\text{Y}_{0.25})_{0.7}\text{Sr}_{0.3}\text{MnO}_3$

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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 crystal and polycrystalline $\text{La}_{0.7}\text{Ca}_{0.3}\text{MnO}_3$, polycrystalline $\text{La}_{0.7}\text{Sr}_{0.3}\text{MnO}_3$ and $(\text{La}_{0.75}\text{Y}_{0.25})_{0.7}\text{Sr}_{0.3}\text{MnO}_3$ has been studied in order to know the influence of grain boundary on magnetoresistance. As a result, the following characteristics are found: (i) Magnetoresistance of polycrystalline $\text{La}_{0.7}\text{Ca}_{0.3}\text{MnO}_3$ and $(\text{La}_{0.75}\text{Y}_{0.25})_{0.7}\text{Sr}_{0.3}\text{MnO}_3$, whose grain sizes are about 10 μm , drastically decreases at a low magnetic field about 200 kA/m (for example, about 20% decrease at 4.2 K), and gradually decreases with increasing magnetic field up to 5.6 MA/m used in the present study, being different in case of single crystal $\text{La}_{0.7}\text{Ca}_{0.3}\text{MnO}_3$. This behaviour of magnetoresistance of the present polycrystalline specimens is quite similar to that of the polycrystalline $\text{La}_{2/3}\text{Sr}_{1/3}\text{MnO}_3$ previously reported and cannot be explained quantitatively by the model proposed by Raychaudhuri *et al.*, which is derived based on the tunneling conduction mechanism through the grain boundary. (ii) Magnetoresistance of $\text{La}_{0.7}\text{Sr}_{0.3}\text{MnO}_3$ extremely depends on the grain size and its absolute value, $|\Delta\rho(T, H)/\rho(T, 0)|$, decreases with increasing the grain size (12 μm , 300 μm , 1200 μm) at 4.2 K in the range of magnetic field up to 5.6 MA/m. A characteristic feature is that there is a similar transformation of magnetoresistance for specimens with different grain sizes. (iii) Time-dependent nature of resistance exists for the present polycrystalline specimens, but not for the single crystal specimen, suggesting that the magnetism around the grain boundary should be a spin-glass like state.

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1. Introduction

Perovskite manganites with 20–40% of trivalent rare-earth metal ions (R^{3+}) replaced by divalent alkaline-earth metal ions (A^{2+}), $R_{1-x}A_x\text{MnO}_3$, have been studied for many years, and many interesting phenomena, such as metal-insulator transition and colossal magnetoresistance, were reported so far.^{1–6)} These phenomena are mainly explained by double-exchange interaction:^{7–12)} magnetic interaction between Mn^{3+} and Mn^{4+} that is caused by the hopping of e_g electrons between the two partially filled d shells with strong on-site Hund's coupling. Besides the above phenomena, polycrystalline manganites show quite interesting magnetoresistance. Incidentally, magnetoresistance originally means a phenomenon concerned with resistance under a magnetic field. However, many researchers in this field^{13–20)} define it as a quantity $\Delta\rho(T, H)/\rho(T, 0) = (\rho(T, H) - \rho(T, 0))/\rho(T, 0)$, where $\rho(T, H)$ and $\rho(T, 0)$ denote the resistivity at a temperature with and without a magnetic field, respectively. In the present study, we follow their definition. Also, we abbreviate magnetoresistance as MR hereafter for simplicity.

Recently, Hwang *et al.*¹³⁾ investigated MR of polycrystalline $\text{La}_{2/3}\text{Sr}_{1/3}\text{MnO}_3$ below Curie temperature T_c and they found that the MR drastically decreases with first increments of magnetic field and gradually decreases with increasing magnetic field. Considering this result, they pointed out the similarity between the MR of polycrystalline specimen and that of granular nickel film.¹⁴⁾ Raychaudhuri *et al.*¹⁵⁾ also investigated MR of polycrystalline $\text{La}_{0.7-x}\text{Ho}_x\text{Sr}_{0.3}\text{MnO}_3$ ($x = 0, 0.15$) and proposed a tunneling model to explain the MR of polycrystalline manganites. However, its propriety

and the mechanism of MR have not been clarified until now. In order to make the mechanism of MR clear, we need more information on MR, that is, whether MR depends on a kind of compounds, or how MR depends on the grain size. As for grain size dependence of MR, there has been no systematic study where the grain size is changed largely.^{13,16–20)}

In the present study, we investigate MR using other typical compounds exhibiting a metal-insulator transition, such as $\text{La}_{0.7}\text{Ca}_{0.3}\text{MnO}_3$ and $(\text{La}_{0.75}\text{Y}_{0.25})_{0.7}\text{Sr}_{0.3}\text{MnO}_3$, in order to obtain more information on MR, that is, whether MR depends on a kind of compounds. We also investigate the grain size dependence of MR using polycrystalline $\text{La}_{0.7}\text{Sr}_{0.3}\text{MnO}_3$ because its grain size can be easily controlled.

2. Experiment

Specimens used in the present study are single crystal and polycrystalline $\text{La}_{0.7}\text{Ca}_{0.3}\text{MnO}_3$, polycrystalline $\text{La}_{0.7}\text{Sr}_{0.3}\text{MnO}_3$ and $(\text{La}_{0.75}\text{Y}_{0.25})_{0.7}\text{Sr}_{0.3}\text{MnO}_3$. Polycrystalline specimens were prepared by conventional solid-state reaction processing in air. High purity La_2O_3 , Y_2O_3 , CaCO_3 , SrCO_3 and Mn_3O_4 powder were mixed to the composition above mentioned, and calcined in air at 1473 K for 12 h. Sintering was carried out in air at 1627 K for 48 h for polycrystalline $\text{La}_{0.7}\text{Ca}_{0.3}\text{MnO}_3$ and 1773 K for 48 h for polycrystalline $\text{La}_{0.7}\text{Sr}_{0.3}\text{MnO}_3$ and $(\text{La}_{0.75}\text{Y}_{0.25})_{0.7}\text{Sr}_{0.3}\text{MnO}_3$ after intermediate grinding. Polycrystalline specimens were cut from sintered disks and their average grain sizes were about 10 μm . In case of $\text{La}_{0.7}\text{Sr}_{0.3}\text{MnO}_3$, we obtained the specimens with two other grain sizes (300 μm , 1200 μm) by partially melting them in the mirror furnace under flowing O_2 atmosphere. Single crystal $\text{La}_{0.7}\text{Ca}_{0.3}\text{MnO}_3$ specimen was prepared by a floating zone method in flowing O_2 atmosphere. All the

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specimens used in the present study were confirmed to be single phases at room temperature by an x-ray diffraction; pseudocubic for $\text{La}_{0.7}\text{Ca}_{0.3}\text{MnO}_3$ and $(\text{La}_{0.75}\text{Y}_{0.25})_{0.7}\text{Sr}_{0.3}\text{MnO}_3$ and rhombohedral for $\text{La}_{0.7}\text{Sr}_{0.3}\text{MnO}_3$. Electrical resistivity was measured by standard four probe method and magnetization was measured by SQUID magnetometer. In MR measurements, current direction was parallel to magnetic field.

Curie temperatures, T_c , are determined by a magnetization measurement, and they are about 240 K for both single crystal and polycrystalline $\text{La}_{0.7}\text{Ca}_{0.3}\text{MnO}_3$, about 220 K for polycrystalline $(\text{La}_{0.75}\text{Y}_{0.25})_{0.7}\text{Sr}_{0.3}\text{MnO}_3$ and 365 K for all $\text{La}_{0.7}\text{Sr}_{0.3}\text{MnO}_3$ with different grain sizes. Incidentally, we don't analyze the oxygen content in the specimens used in the present study, although it was reported to affect the electric and magnetic properties.^{21,22)}

3. Results

3.1 Magnetoresistance of polycrystalline and single crystal $\text{La}_{0.7}\text{Ca}_{0.3}\text{MnO}_3$ and polycrystalline $(\text{La}_{0.75}\text{Y}_{0.25})_{0.7}\text{Sr}_{0.3}\text{MnO}_3$

Magnetoresistance of polycrystalline $\text{La}_{0.7}\text{Ca}_{0.3}\text{MnO}_3$ and $(\text{La}_{0.75}\text{Y}_{0.25})_{0.7}\text{Sr}_{0.3}\text{MnO}_3$ has been investigated by applying magnetic field up to 5.6 MA/m, together with that of single crystal $\text{La}_{0.7}\text{Ca}_{0.3}\text{MnO}_3$ for comparison. The results of single crystal and polycrystalline $\text{La}_{0.7}\text{Ca}_{0.3}\text{MnO}_3$ are shown in Figs. 1(a) and (b), respectively, and that of polycrystalline $(\text{La}_{0.75}\text{Y}_{0.25})_{0.7}\text{Sr}_{0.3}\text{MnO}_3$ is shown in Fig. 1(c). As can be seen from Fig. 1(a), the MR, $\Delta\rho(T, H)/\rho(T, 0)$, for single crystal $\text{La}_{0.7}\text{Ca}_{0.3}\text{MnO}_3$ decreases gradually with increasing magnetic field. On the other hand, it is noted in Figs. 1(b) and (c) that the MR of two polycrystalline specimens are quite different from that of single crystal. That is, the MR of both polycrystalline specimens drastically decrease by the initial increment of magnetic field up to 200 kA/m and its value at 4.2 K is about 20%, and decreases with increasing temperature. When a magnetic field is higher than 200 kA/m, the MR decreases gradually with increasing magnetic field up to 5.6 MA/m. This behaviour of MR is quite similar to that of the polycrystalline $\text{La}_{2/3}\text{Sr}_{1/3}\text{MnO}_3$ previously reported by Hwang *et al.*,¹³⁾ meaning that irrespective of kinds of polycrystalline manganites exhibiting a metal-insulator transition, characteristic behaviour of MR should appear intrinsically.

To obtain more information on MR of polycrystalline specimens, we measured the magnetization curve of the polycrystalline $\text{La}_{0.7}\text{Ca}_{0.3}\text{MnO}_3$ and compared it with its MR, which is shown in Fig. 2. In this figure, magnetization curve and MR of single crystal $\text{La}_{0.7}\text{Ca}_{0.3}\text{MnO}_3$ 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, which will be discussed later.

3.2 Grain size dependence of magnetoresistance

The grain size dependence of MR has been investigated at

Fig. 1 Magnetoresistance as a function of magnetic field up to 5.6 MA/m for (a) single crystal $\text{La}_{0.7}\text{Ca}_{0.3}\text{MnO}_3$, (b) polycrystalline $\text{La}_{0.7}\text{Ca}_{0.3}\text{MnO}_3$ and (c) polycrystalline $(\text{La}_{0.75}\text{Y}_{0.25})_{0.7}\text{Sr}_{0.3}\text{MnO}_3$. The dotted lines in (a) show the calculated magnetoresistances of single crystal $\text{La}_{0.7}\text{Ca}_{0.3}\text{MnO}_3$ by using eq. (3).

4.2 K using $\text{La}_{0.7}\text{Sr}_{0.3}\text{MnO}_3$ with different grain sizes of about 12 μm , 300 μm and 1200 μm . The results are shown in Fig. 3, where MR extremely depends on the grain size, and its absolute value, $|\Delta\rho(T, H)/\rho(T, 0)|$, decreases with increasing the grain size in the present range of magnetic field up to 5.6 MA/m. For these MR, we found an interesting fact that there exists a similar transformation in the MR of specimens with different grain sizes, being expressed as,

$$\left(\frac{\Delta\rho(T, H)}{\rho(T, 0)} \right)_{d_1} = \alpha(d_1, d_2) \cdot \left(\frac{\Delta\rho(T, H)}{\rho(T, 0)} \right)_{d_2}, \quad (1)$$

where d_1 and d_2 are the average grain sizes, and $\alpha(d_1, d_2)$ is the parameter. The values of $\alpha(12\mu\text{m}, 300\mu\text{m})$ and $\alpha(12\mu\text{m}, 1200\mu\text{m})$ are 1.8 and 6.3, respectively. This result indicates that MR of polycrystalline specimens are directly related to the grain size, or the number of grain boundaries where the conductive e_g electrons pass through. However, the physical meaning of this similar transformation has not been clarified yet in the present study.

3.3 Time-dependent nature of resistance

We measured the resistance of the present single crystal and polycrystalline specimens as a function of time after removing a magnetic field from 7.2 MA/m to zero with a sweep rate of 16 kA/(m·s). In the measurement, we take the

Fig. 2 Magnetization curve and (b) magnetoresistance as a function of magnetic field of polycrystalline $\text{La}_{0.7}\text{Ca}_{0.3}\text{MnO}_3$, which are indicated by solid lines, together with those of single crystal $\text{La}_{0.7}\text{Ca}_{0.3}\text{MnO}_3$ for comparison, which are indicated by dotted lines.

Fig. 3 Magnetoresistance as a function of magnetic field up to 5.6 MA/m for polycrystalline $\text{La}_{0.7}\text{Sr}_{0.3}\text{MnO}_3$ with different grain sizes of $12 \mu\text{m}$, $300 \mu\text{m}$ and $1200 \mu\text{m}$. Inset shows a similar transformation in the MR for specimens with different grain sizes by using eq. (1).

starting time ($t = 0$) when the magnetic field is removed to zero. The results of single crystal and polycrystalline $\text{La}_{0.7}\text{Ca}_{0.3}\text{MnO}_3$ and polycrystalline $(\text{La}_{0.75}\text{Y}_{0.25})_{0.7}\text{Sr}_{0.3}\text{MnO}_3$ are shown in Fig. 4(a) and those of polycrystalline $\text{La}_{0.7}\text{Sr}_{0.3}\text{MnO}_3$ with different grain sizes are shown in Fig.

Fig. 4 The change of resistivity, $\Delta\rho(t) / \rho(0)$, as a function of time for (a) single crystal and polycrystalline $\text{La}_{0.7}\text{Ca}_{0.3}\text{MnO}_3$ and polycrystalline $(\text{La}_{0.75}\text{Y}_{0.25})_{0.7}\text{Sr}_{0.3}\text{MnO}_3$ and (b) polycrystalline $\text{La}_{0.7}\text{Sr}_{0.3}\text{MnO}_3$ with different grain sizes of about $12 \mu\text{m}$, $300 \mu\text{m}$ and $1200 \mu\text{m}$, where $\Delta\rho(t) / \rho(0)$ is obtained after removing magnetic field from 7.2 MA/m to zero. Inset shows the ac-susceptibility for polycrystalline $\text{La}_{0.7}\text{Sr}_{0.3}\text{MnO}_3$ with grain size of about $12 \mu\text{m}$ under magnetic field of $H = 160 \text{ A/m}$ with frequencies of 100 Hz, 1000 Hz, and 10000 Hz.

4(b), where the change of resistivity $\Delta\rho(t) = \rho(t) - \rho(0)$ is normalized by the resistivity at $t = 0$, $\Delta\rho(t) / \rho(0)$. As can be seen from Fig. 4(a), $\Delta\rho(t) / \rho(0)$ of the polycrystalline specimens with their grain sizes of about $10 \mu\text{m}$ 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. Moreover, as can be seen in Fig. 4(b), this time-dependent nature is related to the grain size. That is, $\Delta\rho(t) / \rho(0)$ of polycrystalline $\text{La}_{0.7}\text{Sr}_{0.3}\text{MnO}_3$ depends on the grain size and decreases with increasing the grain size.

In this way, in polycrystalline manganites, resistance once experienced an application of a magnetic field has time-dependent nature and depends on the grain size. 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. Then we measured ac- and dc-susceptibilities of the present polycrystalline specimens in order to know the existence of spin-glass like state. The typical result of ac-susceptibility for $\text{La}_{0.7}\text{Sr}_{0.3}\text{MnO}_3$, whose grain size is about $12 \mu\text{m}$, under

magnetic field of $H = 160$ A/m with frequencies of 100 Hz, 1000 Hz, 10000 Hz is shown in the inset of Fig. 4. It is noted that the real part of ac-susceptibility depends on the frequency of magnetic field at temperatures lower than 100 K and there is a bend around 35 K indicated with an arrow, although the imaginary part of ac-susceptibility is unclear to detect the peak associated with a spin-glass state. Moreover, 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. Considering the results described above, we speculate that a spin-glass like state appears around the grain boundary, but not in the grain of the specimen. In addition, if this speculation is right, we can explain that the time-dependent nature is related to the grain size because the value of $\Delta\rho(t)/\rho(0)$ should be proportional to the amount of the grain boundary exhibiting a spin-glass like state.

4. Discussion

In this section, we will analyze the MR of single crystal and polycrystalline $\text{La}_{0.7}\text{Ca}_{0.3}\text{MnO}_3$ and polycrystalline $(\text{La}_{0.75}\text{Y}_{0.25})_{0.7}\text{Sr}_{0.3}\text{MnO}_3$, shown in Fig. 1, based on the models previously reported.^{11,15)}

Searle and Wang¹¹⁾ 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 at a temperature T and a field H , $\rho(T, 0)$, is expressed as,

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

where $M(T, 0)$ is the spontaneous magnetization at a temperature T , N is the density of conductive e_g electrons and C is the constant. Based on eq. (2), we calculated the electrical resistivity of the present single crystal $\text{La}_{0.7}\text{Ca}_{0.3}\text{MnO}_3$ at $T = 4.2, 77, 150$ and 200 K at zero magnetic field. The calculated results are shown in Fig. 5 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 temper-

Fig. 5 Temperature dependence of experimental (solid line) and calculated (open diamonds) resistivities for single crystal $\text{La}_{0.7}\text{Ca}_{0.3}\text{MnO}_3$, where the calculated values are obtained by using eq. (2).

ature, $\rho(T, 0)/\rho(T_c, 0)$, because it is too difficult to evaluate the value of N . The calculated $\rho(T, 0)/\rho(T_c, 0)$ are in good agreement with the experimental ones.

We also analyze the MR of $\Delta\rho(T, H)/\rho(T, 0)$ in the present single crystal by using the following equation, derived by Searle and Wang,¹¹⁾

$$\frac{\Delta\rho(T, H)}{\rho(T, 0)} = \left(\frac{M(0, 0)^2 - M(T, H)^2}{M(0, 0)^2 + M(T, H)^2} \right) \times \left(\frac{M(0, 0)^2 + M(T, 0)^2}{M(0, 0)^2 - M(T, 0)^2} \right) - 1, \quad (3)$$

Where $M(T, H)$ is the magnetization at a temperature T , and a magnetic field H . From eq. (3), we calculated the MR of the single crystal $\text{La}_{0.7}\text{Ca}_{0.3}\text{MnO}_3$, as shown in Fig. 1(a) by dotted curves. The calculated MR of $\Delta\rho(T, H)/\rho(T, 0)$ are in good agreement with experimental ones at magnetic fields lower than 2 MA/m. Considering that eq. (3) 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.¹¹⁾

Next, we will analyze the MR of polycrystalline specimens, based on the model derived by Raychaudhuri *et al.*¹⁵⁾ Their model is derived considering that the drastic decrease of MR at low magnetic field is due to a tunneling conduction mechanism 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,

$$\sigma(T, H) \propto \left(\frac{1}{2} \right) (n_{\uparrow} + n_{\downarrow})^2 [1 + P^2 \cos \theta(T, H)] = \frac{1}{\rho(T, H)}, \quad (4)$$

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. (4), MR of $\Delta\rho(T, H)/\rho(T, 0)$ is expressed as,

$$\frac{\Delta\rho(T, H)}{\rho(T, 0)} = \frac{P^2 \langle \cos \theta(T, 0) \rangle - P^2 \langle \cos \theta(T, H) \rangle}{1 + P^2 \langle \cos \theta(T, H) \rangle}, \quad (5)$$

where $\theta(T, 0)$ is the angle between the magnetic moments of two adjacent grains at zero field and $\langle \cos \theta(T, H) \rangle$ is an average of $\cos \theta(T, H)$. It should be noted in eq. (5) that when the magnetization is saturated, $\langle \cos \theta(T, 0) \rangle$ is only unknown parameter because P and $\Delta\rho(T, H)/\rho(T, 0)$ are obtained experimentally and $\langle \cos \theta(T, H) \rangle$ comes to be 1, considering that the magnetic moments for all the grains are aligned to the magnetic field direction. Then we calculated $\langle \cos \theta(T, 0) \rangle$ as a function of temperature based on eq. (5). The calculated values $\langle \cos \theta(T, 0) \rangle$ of polycrystalline $\text{La}_{0.7}\text{Ca}_{0.3}\text{MnO}_3$ and $(\text{La}_{0.75}\text{Y}_{0.25})_{0.7}\text{Sr}_{0.3}\text{MnO}_3$ are shown in Fig. 6, where $\langle \cos \theta(T, 0) \rangle$ for both specimens increase with increasing temperature. This temperature dependence of $\langle \cos \theta(T, 0) \rangle$ contradicts with the fact that $\langle \cos \theta(T, 0) \rangle$ reasonably depends only on the configuration of grain, and therefore it does not depend on temperature. Thus, the MR of polycrystalline

Fig. 6 Temperature dependence of $\langle \cos \theta(T, 0) \rangle$ for polycrystalline $\text{La}_{0.7}\text{Ca}_{0.3}\text{MnO}_3$ (open circles) and $(\text{La}_{0.75}\text{Y}_{0.25})_{0.7}\text{Sr}_{0.3}\text{MnO}_3$ (open squares), which are obtained by using eq. (5).

manganites investigated in the present study cannot be explained by the above model proposed by Raychaudhuri *et al.*¹⁵⁾

When a magnetic field is higher than 200 kA/m, MR of polycrystalline specimens decreases gradually with increasing magnetic field up to 5.6 MA/m, as mentioned before. 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 can conclude from the results described above that there needs a new model which can be explained quantitatively the MR of polycrystalline manganite, and this is the future problem.

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