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# The influence of grain boundaries on the magnetoresistance in $La_{0.7}A_{0.3}MnO_3$ (A = Ca, Sr) and $La_{1.36}Sr_{1.64}Mn_2O_7$

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**Abstract**

The influence of grain boundaries on the magnetoresistance in the perovskite manganites $La_{0.7}A_{0.3}MnO_3$ (A = Ca, Sr) and the layered perovskite manganites $La_{1.36}Sr_{1.64}Mn_2O_7$ has been investigated by means of ac and dc magnetic susceptibility and magnetoresistance measurements. The following characteristics were found. (i) The magnetoresistance (MR) of single-crystal $La_{0.7}Ca_{0.3}MnO_3$ is almost independent of the magnetic field at low temperatures, and the MR of polycrystalline $La_{0.7}A_{0.3}MnO_3$ (A = Ca, Sr) and $La_{1.36}Sr_{1.64}Mn_2O_7$ decreases drastically with the initial increment of the magnetic field up to $2.5 \times 10^{-1}$ T. (ii) The resistivity and the absolute value of the MR of polycrystalline $La_{0.7}Sr_{0.3}MnO_3$ increase with decreasing grain size at 4.2 K. (iii) The resistivity of these polycrystalline manganites shows a time-dependent nature, but the single-crystal form does not.

## 1. Introduction

The perovskite manganites $R_{1-x}A_xMnO_3$ ($0.2 < x < 0.4$) show many interesting phenomena, such as metal–insulator transition and colossal magnetoresistance. Therefore, they have been studied extensively for many years. These phenomena are mainly explained by the double-exchange interaction [1–4].

Recently, Hwang *et al* [5] investigated the magnetoresistance (MR) of polycrystalline $La_{2/3}Sr_{1/3}MnO_3$ below the Curie temperature $T_C$, and pointed out that there is a similarity between the MR of polycrystalline specimens 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 tunnelling model to explain the behaviour of the MR of polycrystalline specimens. However, there have not been many studies of the MR for polycrystalline manganites, and the mechanism of the MR has not been made clear so far. In order to make this mechanism clear, we need more information on the MR for many compounds. In the present study, we investigate the MR of polycrystalline $La_{0.7}A_{0.3}MnO_3$ (A = Ca, Sr) and polycrystalline $La_{1.36}Sr_{1.64}Mn_2O_7$ which shows layered perovskite structure [8], and investigate the MR of single-crystal $La_{0.7}Ca_{0.3}MnO_3$ for comparison.

## 2. Experimental procedure

Polycrystalline $La_{0.7}A_{0.3}MnO_3$ (A = Ca, Sr) and $La_{1.36}Sr_{1.64}Mn_2O_7$ were prepared by conventional solid state reaction processing. Single-crystal $La_{0.7}Ca_{0.3}MnO_3$ was prepared by the floating zone method. The electrical resistivity was measured by the standard four-probe method. The dc and ac susceptibility were measured by a SQUID magnetometer. The amplitude of ac field is 2 Oe and dc bias field is zero. The temperatures of the transitions from ferromagnetic metal to paramagnetic insulator for $La_{0.7}A_{0.3}MnO_3$ (A = Ca, Sr) and $La_{1.36}Sr_{1.64}Mn_2O_7$ are about 250, 365 and 125 K, respectively. In the MR measurements, the current direction was parallel to the magnetic field. The nature of the resistivity was measured as a function of time upon decreasing a magnetic field from 9 T to zero with a sweep rate of $2.0 \times 10^{-2}$ T s$^{-1}$.

## 3. Results

The MR of single-crystal and polycrystalline $La_{0.7}Ca_{0.3}MnO_3$ and polycrystalline $La_{1.36}Sr_{1.64}Mn_2O_7$ were measured by applying magnetic fields up to 7 T below each Curie temperature, where the MR is defined as $\Delta\rho(T, H)/\rho(T, 0) = (\rho(T, H) - \rho(T, 0))/\rho(T, 0)$, and $\rho(T, H)$ denotes the resistivity at a temperature $T$ with a magnetic field $H$. The results on single-crystal and polycrystalline $La_{0.7}Ca_{0.3}MnO_3$ for both increasing and decreasing field processes are shown in figures 1(a) and (b), respectively. The inset of figure 1(a) shows the magnetization curve of single-crystal $La_{0.7}Ca_{0.3}MnO_3$. The results for polycrystalline $La_{1.36}Sr_{1.64}Mn_2O_7$ are shown in figure 1(c). Figure 1(a) shows that the MR decreases slightly at lower temperatures ($T = 4.2$ and 77 K), and the MR decreases gradually with increasing magnetic field at higher temperatures ($T = 150$ and 200 K). On the other hand, it is noted in figures 1(b) and (c) that the MR of two polycrystalline specimens are quite different from that of the single-crystal one. That is, the MR of polycrystalline $La_{0.7}Ca_{0.3}MnO_3$ decreases drastically with the initial increment of the magnetic field up to $2.5 \times 10^{-1}$ T and the value at 4.2 K is about $-0.2$, and decreases with increasing temperature. When the magnetic field is higher than $2.5 \times 10^{-1}$ T, the MR decreases gradually with increasing magnetic field up to 7 T, and its value is about $-0.4$ at 4.2 K. The MR of $La_{1.36}Sr_{1.64}Mn_2O_7$ also decreases drastically with the field up to $2.5 \times 10^{-1}$ T and its value is about $-0.3$ at 4.2 K; and when the magnetic field is higher than $2.5 \times 10^{-1}$ T, the MR decreases gradually with increasing magnetic field up to 7 T and its value is about $-0.6$ at 4.2 K. The MR of $La_{1.36}Sr_{1.64}Mn_2O_7$ at 4.2 K only shows hysteresis. These MR behaviours of the two polycrystalline manganites resemble each other and they are similar to the behaviour in the previous studies [5, 7].

The grain size dependence of the magnetoresistance has been investigated at 4.2 K by using $La_{0.7}Sr_{0.3}MnO_3$ with different grain sizes of about 1200, 300 and 12 $\mu$m. The results are shown in figures 2(a) and (b). It is noted in figure 2(a) that the MR of polycrystalline specimens increases with decreasing grain size. The grain size dependence of the resistivity, $\rho$, and the decrease of the resistivity, $|\Delta\rho(4.2\ \mathrm{K}, 7\ \mathrm{T})|$, is shown in figure 2(b). The grain size, $d$, is defined as the length of a line drawn between the voltage terminals divided by the number of grain boundaries across the line. We found that the values of $\rho$ and $|\Delta\rho(4.2\ \mathrm{K}, 7\ \mathrm{T})|$ are

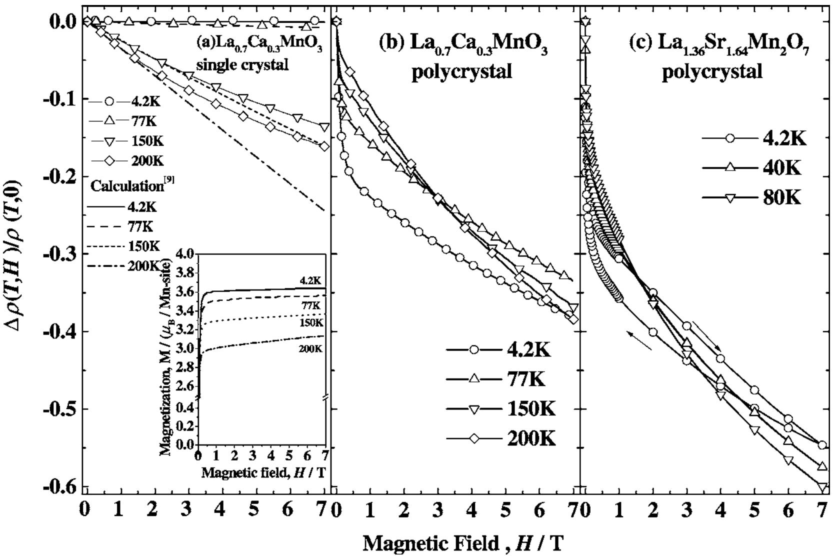


**Figure 1.** Magnetoresistance as a function of magnetic field up to 7 T for (a) single-crystal $La_{0.7}Ca_{0.3}MnO_3$, (b) polycrystalline $La_{0.7}Ca_{0.3}MnO_3$ and (c) polycrystalline $La_{1.36}Sr_{1.64}Mn_2O_7$. The dotted lines in (a) show the calculated magnetoresistances for single-crystal $La_{0.7}Ca_{0.3}MnO_3$ obtained by using the model of Searle and Wang [9]. The inset shows the magnetization curves for single-crystal $La_{0.7}Ca_{0.3}MnO_3$.

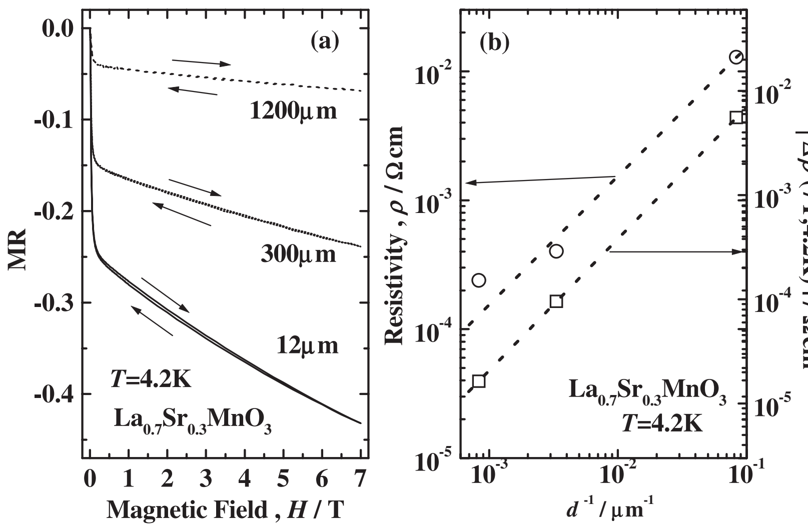


**Figure 2.** The grain size dependence of (a) the MR and (b) the resistivity at zero field and $|\Delta\rho(4.2\ \mathrm{K}, 7\ \mathrm{T})|$ for polycrystalline $La_{0.7}Sr_{0.3}MnO_3$ at 4.2 K.

almost proportional to the reciprocal of grain size which is closely related to the number of times the conductive $e_g$ electrons pass through the grain boundary.

As regards the resistivities of polycrystalline manganites, it is found that they show a time-dependent nature. The time-dependent natures of polycrystalline $La_{0.7}Sr_{0.3}MnO_3$ and $La_{1.36}Sr_{1.64}Mn_2O_7$ are shown in figure 3, where the change in resistivity is defined as

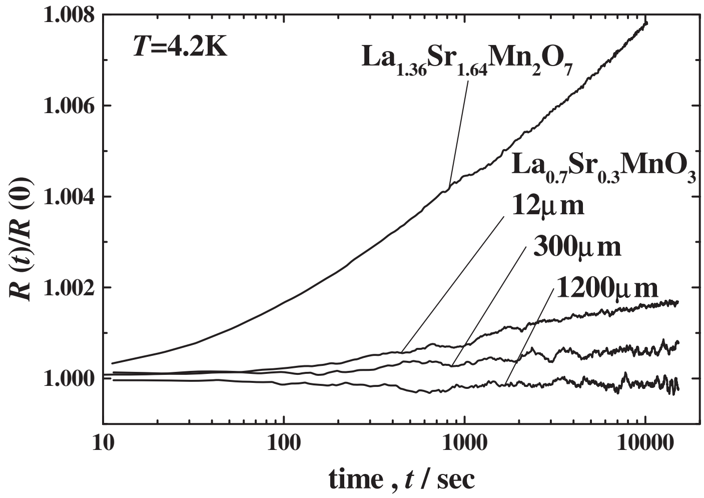


**Figure 3.** The change of resistivity, $\Delta\rho(t)/\rho(t=0)$, as a function of time for polycrystalline $La_{0.7}Sr_{0.3}MnO_3$ and polycrystalline $La_{1.36}Sr_{1.64}Mn_2O_7$, where $\Delta\rho(t)/\rho(t=0)$ is obtained after decreasing the magnetic field from 9 T to zero.

$\Delta\rho(t)/\rho(t=0) = (\rho(t)-\rho(t=0))/\rho(t=0)$, and $t$ is the time after removing the magnetic field. As shown in figure 3, $\Delta\rho(t)/\rho(t=0)$ for polycrystalline specimens (300 and 12 $\mu$m) gradually increases as time passes and it depends on the grain size. The origin of this time-dependent nature is not known yet, but it is speculated to be related to the magnetism. Then, we measured the ac and dc susceptibility of $La_{0.7}Sr_{0.3}MnO_3$ and the results are shown in figures 4(a) and (b), respectively. It is noted that the ac susceptibility depends on the frequency of the magnetic field at temperatures lower than about 60 K and there is a bend at around 30 K, and the dc susceptibility of the zero-field cooling process is different from that of the field cooling process at temperatures lower than about 30 K. We speculate that a small amount of spin-glass-like state may appear around a grain boundary which has many defects, but not in each grain.

## 4. Discussion

In order to analyse the MR of single-crystal specimens, we will calculate the MR of single-crystal $La_{0.7}Ca_{0.3}MnO_3$ by using the model previously reported by Searle and Wang [9]. According to their model, the MR can be expressed as

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

where $M(T,H)$ is the magnetization at temperature $T$ and magnetic field $H$. From equation (1), we calculated the MR of the single-crystal $La_{0.7}Ca_{0.3}MnO_3$, as shown in figure 1(a). As seen in the figure, the calculated MR, $\Delta\rho(T,H)/\rho(T,0)$, are in good agreement with experimental ones at lower magnetic fields ($H \leqslant 2$ T). Considering that equation (1) is adequate at lower magnetic fields, we can say that the MR of the single-crystal specimen is explained quantitatively by the model of Searle and Wang [9].

Next, we will analyse the MR of polycrystalline specimens. As mentioned before, the value of $\rho$ is almost proportional to the reciprocal of the grain size. This suggests that the

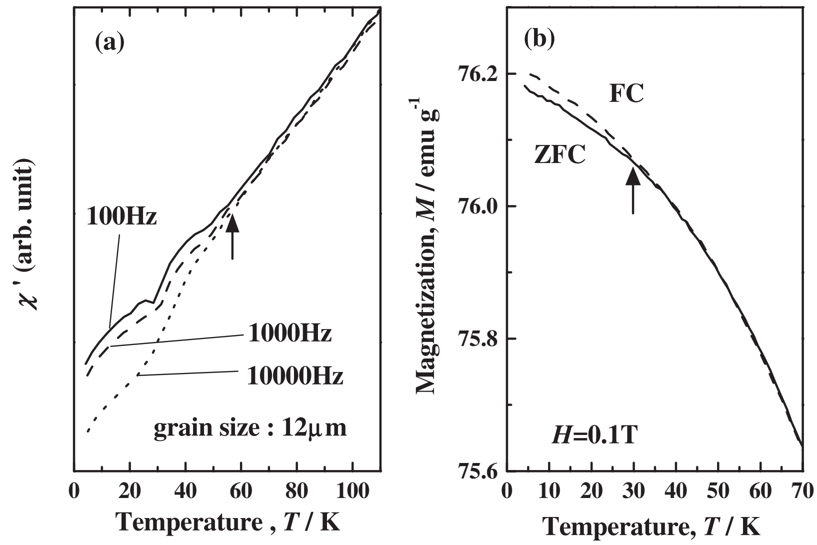


**Figure 4.** The ac susceptibility (a) and dc susceptibility (b) of polycrystalline $La_{0.7}Sr_{0.3}MnO_3$.

resistivity of polycrystalline specimens can be approximated as the series connection of those of grains and grain boundaries. Therefore, we can regard the MR of polycrystalline specimens as the MR of grain boundaries when the number of grain boundaries in the specimen is very large. According to the model of Raychaudhuri *et al* [7], the MR of the grain boundary at low magnetic field ($H \leqslant 2.5 \times 10^{-1}$ T) can be expressed as

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

where $P$ is the polarization of $e_g$ electrons at the Fermi surface, $\theta(T,H)$ is the angle between the magnetic moments of two adjacent grains at magnetic field $H$ and $\langle\cos\theta(T,H)\rangle$ is the average of $\cos\theta(T,H)$. It should be noted in equation (2) that the values of $P$ were reported previously [10] and $\theta(T,H)$ comes to be zero when the magnetization is saturated. If we assume that $\langle\theta(T,0)\rangle$ is 90°, which is the value expected for the random arrangement of magnetic moments, $\Delta\rho(T, 2.5\times10^{-1}\ \mathrm{T})/\rho(T,0)$ will be about $-0.38$. This value is smaller than the experimental value, $-0.24$, for 12 $\mu$m of polycrystalline $La_{0.7}Sr_{0.3}MnO_3$. To analyse this more quantitatively, one needs to measure the direction of magnetization for each grain. However, this is a future problem.

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