Magnetoresistance in thin films and bulks of layered-perovskite $La_{2-2x}Ca_{1+2x}Mn_2O_7$

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Epitaxial thin-film and polycrystalline bulk samples of ferromagnetic $La_{2-2x}Ca_{1+2x}Mn_2O_7$ ($x=0.3$) with a layered perovskite structure have been examined with respect to their magnetotransport properties. In addition to a large magnetoresistance (MR) effect at temperatures around the metal–insulator transition, a-axis thin films exhibit unusual low-temperature MR behavior with apparent hysteresis in applied magnetic fields. The features in the bulk samples are a low-temperature MR effect without such hysteresis, and also an MR effect at high temperatures well above the metal–insulator transition temperature. The unique MR behavior depending on the sample form would reflect an anisotropic nature in the layered-perovskite ferromagnet with two-dimensional Mn-O networks.
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The discovery of the colossal magnetoresistance (CMR) effect in rare-earth manganate perovskites has aroused considerable interest in scientific studies and potential technological applications. These effects have been observed in polycrystalline, single-crystal, and thin-film samples. The magnetic and electronic properties have been examined within the framework of the double-exchange theory,[1,2] which is based on the exchange of electrons between Mn^{3+} and Mn^{4+} ions. So far, most of the experimental work on the CMR phenomena of manganese compounds has been devoted to ABO_3-type cubic (or pseudocubic) perovskites with three-dimensional Mn-O networks, i.e., $Ln_{1-x}M_xMnO_3$ (Ln being rare-earth ions and M divalent cations), such as $La_{1-x}Ca_xMnO_{3-y}$ and $La_{1-x}Sr_xMnO_{3-y}$.[3–11] Such studies have shown that the microstructure of the Mn-O network (the bending of the Mn–O–Mn bond) plays a crucial role with respect to the CMR effect. A decrease in resistance of more than 99% in an applied magnetic field has been reported in thin films of this type of compound,[9] although the magnetic fields producing such large magnetoresistance (MR) effects are as high as several Tesla. Therefore, the challenge of controlling and improving MR in perovskite still remains.

Recently, investigations have shown that magnetoresistance effects occur in ferromagnetic $(La\text{-}M)_3Mn_2O_7$ (M$=$Sr, Ca)[12,13] with a tetragonal $Sr_3Ti_2O_7$-type layered-perovskite structure. Studies on single crystals and polycrystalline bulk samples have shown that the reduced dimensionality of the Mn–O–Mn networks leads to several intriguing changes in features of the ferromagnetic manganate perovskites. These include enhanced MR effects, anisotropic transport in charge carriers, and the appearance of two types of ferromagnetic ordering. Since $(La\text{-}M)_3Mn_2O_7$ is an anisotropic system, epitaxial thin films are essential with a view to a further understanding and future applications of the MR effects in this compound.

In this letter, we report results on the MR properties of epitaxial film and polycrystalline bulk samples of ferromagnetic $La_{2-x}Ca_{1+2x}Mn_2O_7$ ($x=0.3$) with a layered-perovskite structure. Large magnetoresistance (MR) effect at temperatures around the metal–insulator transition was observed for both samples. Moreover, a-axis thin films exhibited unusual low-temperature MR behavior with apparent hysteresis as regards applied magnetic fields. The features in the bulks are a low-temperature MR effect without such hysteresis, and also an MR effect at high temperatures well above the metal–insulator transition temperature. Unusual low-temperature MR behavior showing the hysteresis for thin films and a MR effect at high temperatures well above the metal–insulator transition temperature for the bulk are associated with the existence of two-dimensional and anisotropic Mn-O networks in the layered-perovskite ferromagnet.

The bulk samples were synthesized by a standard ceramic technique, and a single-target magnetron sputtering technique was used for preparing the films. Both preparation methods have been reported in detail, elsewhere.[13,14] The bulk and thin-film samples in this study had a stoichiometric composition with $La_{2-x}Ca_{1+2x}Mn_2O_y$ ($x=0.3$), which was confirmed by energy dispersive x-ray microanalysis (EDX) within the accuracy ($\sim$2%) of EDX. Film thicknesses were 100–300 nm, and substrates used were MgO(001). The structure and orientation of the films were examined by x-ray diffraction with Cu $K\alpha$ radiation. This diffraction study indicated that the crystal structure of the bulk samples were of single phase with the $Sr_3Ti_2O_7$-type tetragonal perovskite structure having the lattice parameters $a_0=0.3864$ nm and $c_0=1.924$ nm. From a diffraction analysis using a four-axis technique, thin films in this study were found to have an a-axis normal orientation with the c axis ordered in the plane and consisted of two domains, rotated at 90° to each other in the plane (the so-called mosaic structure). The lattice parameters a_0 for the films were typically 0.3860–0.3868 nm, which are similar to the bulk value. The electrical resistivity was measured as a function of temperature and magnetic field using the standard four-point technique. Data were collected between 4.2 and 300 K in magnetic fields up to 1.8 T. The field was applied parallel to the sample surface. The MR ratio is usually defined as $-\Delta\rho/\rho_0=-(\rho_H-\rho_0)/\rho_0$

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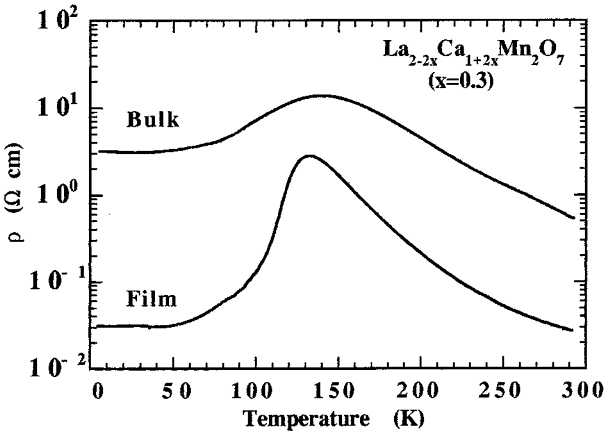

FIG. 1. Temperature dependence of resistivity ρ for thin-film and bulk samples of $La_{2-2x}Ca_{1+2x}Mn_2O_7$ ($x=0.3$). Resistivity ρ is plotted on a logarithmic scale.

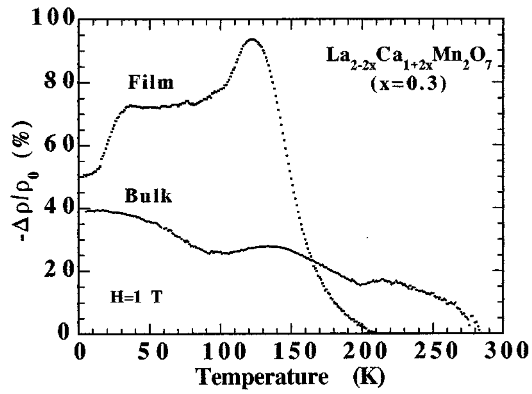

FIG. 2. Temperature dependence of the MR ratio ($-\Delta\rho/\rho_0$) in $\mu_0 H=1$ T for thin-film and bulk samples of $La_{2-2x}Ca_{1+2x}Mn_2O_7$ ($x=0.3$).

(where ρ_H and ρ_0 are the resistivity in an applied magnetic field and the zero-field resistivity, respectively).

In Fig. 1, we show the temperature dependence of the resistivity ρ for thin-film and bulk samples of $La_{2-x}Ca_{1+2x}Mn_2O_7$ ($x=0.3$). There is a peak in the ρ-T curves for both samples with metallic behavior below and semiconducting behavior above this temperature. Hereafter, we refer to the peak temperature in resistivity as $T_\rho^{\max}$. The $T_\rho^{\max}$ value of the thin film was 133 K, which is in good agreement with that (140 K) of the bulk sample. This good agreement between the values ensures the stoichiometry, that is, an appropriate doping concentration (composition and oxygen content). The resistivities ρ of the thin film were much smaller (by one order of magnitude at room temperature and around $T_\rho^{\max}$ and by two orders of magnitude at 4.2 K) than those of the bulk sample. This is mainly attributable to the great reduction in grain-boundary scattering in film samples with epitaxial quality.

The application of a magnetic field resulted in a large reduction in ρ for these samples of $La_{2-2x}Ca_{1+2x}Mn_2O_7$ ($x=0.3$). The temperature dependence of the MR ratio $-\Delta\rho/\rho_0(\mu_0 H=1$ T) for the thin-film and bulk samples are compared in Fig. 2. There are clear differences between the temperature-dependent MR behavior of the thin film and that of the bulk. These differences can be summarized into three typical aspects, that is, (1) MR at $T_\rho^{\max}$, (2) MR at temperatures above ~200 K, and (3) MR at temperatures below ~100 K. With the thin film, the largest MR effect is observed at around $T_\rho^{\max}$ (133 K) and the maximum MR ratio is 93%. In the MR-T curve for the bulk, at around $T_\rho^{\max}$ (140 K) we observed a second maximum with a $-\Delta\rho/\rho_0$ of 30%. With regard to the MR effect at temperatures above ~200 K, the bulk sample exhibited a small but significant MR effect up to room temperature. In contrast, the thin film showed no MR effect in this temperature range. In the low-temperature range well below $T_\rho^{\max}$, there was also an MR effect with an appreciable MR ratio for both the bulk and thin-film samples. At 4.2 K, the $-\Delta\rho/\rho_0$ values for the thin film and bulk were 50% and 38%, respectively.

This complicated temperature-dependent MR behavior of the thin-film and bulk samples is very interesting when we consider the possible mechanism of MR effects in $La_{2-2x}Ca_{1+2x}Mn_2O_7$ with the two-dimensional anisotropic Mn-O networks. Here, a knowledge of the thin film and bulk data for $La_{1-x}Ca_xMnO_{3-y}$ with three-dimensional, isotropic Mn-O networks would be very useful. First, we consider MR at $T_\rho^{\max}$. It is well known that in conventional double-exchange ferromagnets such as $La_{1-x}Ca_xMnO_{3-y}$, CMR is obtained at temperatures where a ferromagnetic metal to paramagnetic insulator transition takes place. In this sense, the MR effects observed in $La_{2-2x}Ca_{1+2x}Mn_2O_7$ at $T_\rho^{\max}$ can be understood by the double exchange models. That is, an external magnetic field tends to align the local spin and then the conduction electrons (holes) with forced spin-polarization suffer less from scattering by local spins. Enlarged MR at $T_\rho^{\max}$ in the thin films compared with that of the bulk was also reported for $La_{1-x}Ca_xMnO_{3-y}$, even when the thin films and the bulks possessed nearly identical hole concentration, namely, identical $T_\rho^{\max}$ value. The enlarged MR effect at around $T_\rho^{\max}$ for the thin films is possibly due to an increased contribution by the spin dependent transport, resulting from the reduction in spin-independent transport at grain boundaries and defects.

Next, we consider the high-temperature (>200 K) MR effect which is evident in bulk samples of $La_{2-x}Ca_{1+2x}Mn_2O_7$. In this respect, it seems essential to consider the magnetic properties of the samples. In $(La\text{-}M)_3Mn_2O_7$ (M=Sr,Ca) system with the anisotropic Mn-O networks, the appearance of two types of ferromagnetic ordering, which possibly originate from the anisotropic exchange interaction, has been suggested from a previous study.[13] Because of this phenomenon, there is a large deviation between experimentally observed $T_\rho^{\max}$ and T_c in bulk $La_{2-2x}Ca_{1+2x}Mn_2O_7$. From magnetization data in a magnetic field of $\mu_0 H=1$ T, the bulk ferromagnetic transition for the present bulk sample ($x=0.3$) occurred at 251 K, which is about 100 K higher than the $T_\rho^{\max}$ value (140 K). In contrast, the temperature dependence of magnetization for the thin films was somewhat different. The magnetization of the thin films dropped most steeply at around 130 K, which is very close to the $T_\rho^{\max}$ value (133 K), and a small but definite magnetization remained in the higher temperature range. High-temperature susceptibility measurement of the

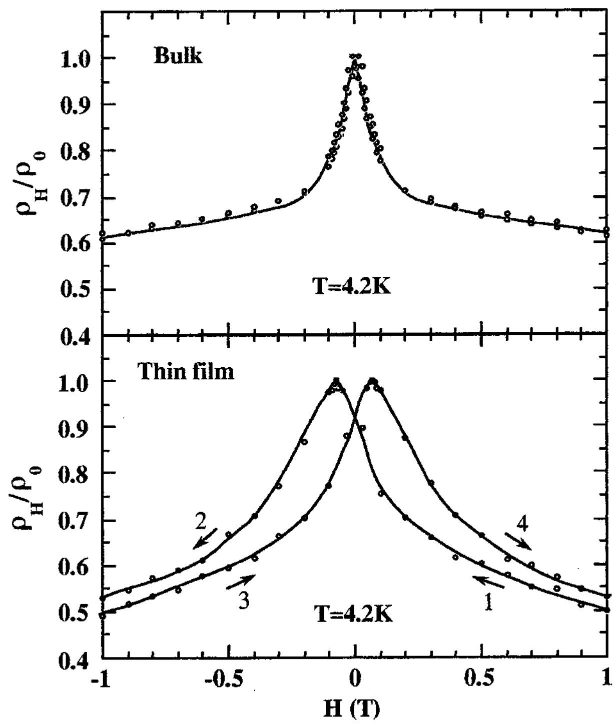

FIG. 3. Normalized resistivity ρ_H/ρ_0 as a function of applied magnetic field at 4.2 K for thin film and bulk $La_{2-2x}Ca_{1+2x}Mn_2O_7$ ($x=0.3$). The data were obtained after an initial application of a magnetic field of $+1.8$ T and sampling cycles are shown as arrows. The solid lines are drawn only as a guide to the eyes.

thin film showed that the paramagnetic Curie temperature is 250 K, which is close to the measured ferromagnetic transition temperature for the bulk sample. The differences observed in the magnetization behavior of the thin-film and bulk samples could be understood by taking into consideration the magnetization process of the anisotropic properties of the present compound. Thus, the absence of an MR effect in the thin film in this higher temperature range seems to be related to the magnetization behaviors.

It should be noted that the most striking feature of $La_{2-2x}Ca_{1+2x}Mn_2O_7$ is its low-temperature MR behavior. In the case of $La_{1-x}Ca_xMnO_3$ with isotropic Mn-O networks, only the bulk samples exhibited large MR effects at low temperatures and very low fields. This can be associated with magnetic-domain based scattering,[10,15] or spin-polarized tunneling between grains.[16] Thus, this type of low-temperature MR behavior could not be observed for single crystals or epitaxial thin films of $La_{1-x}Ca_xMnO_3$. In contrast, with $La_{2-x}Ca_{1+2x}Mn_2O_7$, the present thin-film and bulk data were quite different. We observed an appreciable MR effect not only for the bulk but also for the thin-film samples. We examined the field dependence of normalized resistivity for thin film and bulk $La_{2-x}Ca_{1+2x}Mn_2O_7$ at 4.2 K and the results are shown in Fig. 3. This measurement was performed after an initial application of a magnetic field of $+1.8$ T. Here, we demonstrated that the magnetic field dependence of magnetization (not shown) is nearly identical for both samples. It should be noted that considerable hysteresis can be seen in the resistivity versus magnetic-field curve for the thin film. However, the bulk samples exhibits almost no such hysteresis, and the field dependence of its resistivity is very similar to that reported for $La_{1-x}Ca_xMnO_3$ bulk, suggesting that the MR is mainly due to a grain boundary tunneling, or scattering, mechanism. The hysteresis curve for the thin films is reminiscent of the spin-polarized tunneling effects in the ferromagnet/insulator/ferromagnet structure.[17,18] Since $La_{2-x}Ca_{1+2x}Mn_2O_7$ consists of stacked layers between metallic $(MnO_2)_2$ layer and an insulating $La(Ca)_2O_2$ layer, *intrinsic* spin-polarized tunneling phenomena, which resemble the intrinsic Josephson effect[19] in stacked layers in high-T_c copper oxide perovskites, could be assumed for the compound. Because a-axis films consist of c-axis domains in the film plane, the in-plane transport can be consistently interpreted in view of the intrinsic tunneling effect in the c-axis direction.

In conclusion, we have presented MR data on thin-film and bulk samples of ferromagnetic $La_{2-x}Ca_{1+2x}Mn_2O_7$ with two-dimensional Mn-O networks. A large and fundamental difference can be seen between the temperature-dependent MR behavior of the two types of sample. A characteristic low-temperature MR effect, which has been observed in the in-plane transport of a-axis thin films, is unique for this compound. Further study is necessary to elucidate the mechanism for the magnetotransport properties of ferromagnetic perovskites with two-dimensional Mn-O networks. Thin films of this type of ferromagnetic compound exhibiting low-field MR effects may be useful for future MR applications.

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