



Giant magnetoresistance of a two-dimensional ferromagnet $\text{La}_{2-2x}\text{Ca}_{1+2x}\text{Mn}_2\text{O}_7$

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Giant magnetoresistance of a two-dimensional ferromagnet

$\text{La}_{2-2x}\text{Ca}_{1+2x}\text{Mn}_2\text{O}_7$

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Bulk samples of $\text{La}_{2-2x}\text{Ca}_{1+2x}\text{Mn}_2\text{O}_7$ with the layered $\text{Sr}_3\text{Ti}_2\text{O}_7$ -type perovskite structure have been successfully synthesized and investigated with respect to their magnetic and electrical properties. It is found that $\text{La}_{2-2x}\text{Ca}_{1+2x}\text{Mn}_2\text{O}_7$ ($x=0.25$) is a metallic ferromagnet with a magnetic transition temperature T_c of 215 K. The large magnetoresistance (MR) effect with $\Delta\rho/\rho_0$ of $\sim 60\%$ at 1.8 T was observed in a wide temperature range below a cusp temperature in resistivity of 96 K, which is well below the magnetic T_c . This behavior is quite different from that of the well-known double-exchange ferromagnets such as $\text{La}_{1-x}\text{Ca}_x\text{MnO}_3$, where large MR effects are restricted to a narrow temperature range around the ferromagnetic transition. The present result could be interpreted by using the double-exchange theory incorporating the anisotropy resulting from the two-dimensional Mn-O-Mn networks in $\text{La}_{2-2x}\text{Ca}_{1+2x}\text{Mn}_2\text{O}_7$. © 1996 American Institute of Physics. [S0003-6951(96)00825-X]

Since the discovery of high-temperature superconductivity, there has been renewed interest in mixed-valence perovskite 3d-transition-metal systems with strong electron correlations. Among a number of perovskite compounds, hole-doped manganese oxide systems have attracted great attention because of their particular magnetotransport phenomena resulting from strong spin-charge coupling. The ABO_3 -type compounds with three-dimensional Mn-O-Mn networks, $\text{Ln}_{1-x}\text{M}_x\text{MnO}_3$ (Ln being rare-earth ions and M divalent cations), such as $\text{La}_{1-x}\text{Ca}_x\text{MnO}_3$ and $\text{La}_{1-x}\text{Sr}_x\text{MnO}_3$, have long been known to be conducting ferromagnets. The magnetic interaction is commonly accepted as being the result of double-exchange mechanisms based on the mixed $\text{Mn}^{3+}/\text{Mn}^{4+}$ valence state.¹⁻⁴ With the ABO_3 -type manganese oxides, a ferromagnetic metal to a paramagnetic insulator transition take place at a magnetic transition temperature T_c at which large negative magnetoresistance effects have been observed.⁵⁻¹¹

Other variations of perovskite oxide compounds are known to exist, and the general formula is $\text{A}_{n+1}\text{B}_n\text{O}_{3n+1}$. Apart from ABO_3 -type ($n=\infty$) manganese oxides, $\text{A}_{n+1}\text{B}_n\text{O}_{3n+1}$ -type compounds have layered perovskite structures with two- or quasi-two-dimensional Mn-O-Mn networks. For such compounds, the magnetotransport phenomena arising from the mixed $\text{Mn}^{3+}/\text{Mn}^{4+}$ valence state are expected to be interesting in terms of anisotropic transport and exchange interactions. So far, the manganese oxide with $n=1$, $\text{La}_{1-x}\text{Sr}_{1+x}\text{MnO}_4$ with a layered perovskite structure (K_2NiF_4 type), has been examined and found to be two-dimensional antiferromagnets.^{12,13} Much more recently, a study on single crystals has shown that the manganese oxide with $n=2$, $\text{La}_{2-2x}\text{Sr}_{1+2x}\text{Mn}_2\text{O}_7$ ($x=0.4$) is a conducting ferromagnet.¹⁴

In this letter, we report the magnetic and electrical properties of layered perovskite $\text{La}_{2-2x}\text{Ca}_{1+2x}\text{Mn}_2\text{O}_7$ with two-dimensional Mn-O-Mn networks. Bulk samples of $\text{La}_{2-2x}\text{Ca}_{1+2x}\text{Mn}_2\text{O}_7$ ($x=0.25$) exhibit large negative magnetoresistance ($\Delta\rho/\rho_0=64\%$ at $\mu_0H=1.8$ T) at a temperature (77 K) which is much lower than its magnetic transition

temperature ($T_c=215$ K). This behavior is quite different from that of three-dimensional double-exchange ferromagnets such as $\text{La}_{1-x}\text{Ca}_x\text{MnO}_3$, where the magnetic transition temperature is nearly the same as the metal-insulator transition temperature. This behavior is considered to be closely connected to an anisotropic exchange interaction resulting from the two-dimensional Mn-O-Mn networks in $\text{La}_{2-2x}\text{Ca}_{1+2x}\text{Mn}_2\text{O}_7$.

Bulk ceramic samples were prepared by a standard ceramic process. Stoichiometric amounts of La_2O_3 , CaCO_3 , and Mn_2O_3 were mixed, ground, and calcined at 900 °C for 20 h in an O_2 atmosphere. The samples were sintered at temperatures in the 1400–1450 °C range for 20 h in an O_2 gas atmosphere. We characterized the samples using x-ray diffraction and energy dispersive x-ray microanalysis (EDX). The composition was found to be nearly identical to the nominal one within the accuracy ($\sim 2\%$) of EDX. The electrical resistance and magnetoresistance were measured as a function of temperature and magnetic field by a standard four-point technique. The magnetization was measured on a vibrating sample magnetometer. The MR ratio is defined as $\Delta\rho/\rho_0=(\rho_0-\rho)/\rho_0$ (where ρ and ρ_0 are the resistivity at an applied magnetic field and the zero field resistivity, respectively).

Figure 1 shows the x-ray diffraction pattern for a bulk sample of $\text{La}_{2-2x}\text{Ca}_{1+2x}\text{Mn}_2\text{O}_7$ ($x=0.25$). All the diffraction peaks are indexed with the $\text{Sr}_3\text{Ti}_2\text{O}_7$ -type perovskite. The good agreement obtained between the calculated and observed relative line intensities indicates that the sample is nearly single phase of the $\text{Sr}_3\text{Ti}_2\text{O}_7$ -type structure, and is not a mixture with the ABO_3 - and K_2NiF_4 -type structures. In Fig. 2, we show the crystal structure of $\text{La}_{2-2x}\text{Ca}_{1+2x}\text{Mn}_2\text{O}_7$, which is the tetragonal structure with the $\text{Sr}_3\text{Ti}_2\text{O}_7$ -type perovskite.¹⁵ The space group is I4/mmm . The lattice parameters of the tetragonal unit cell for the sample ($x=0.25$) are $a=0.3872$ nm and $c=1.9248$ nm. In this system, the double perovskite layers are interleaved with $\text{La}(\text{Ca})\text{O}$ layers, and Mn-O-Mn bonds in the c -axis direction are separated from one another by the $\text{La}(\text{Ca})\text{O}$ layers. Thus,

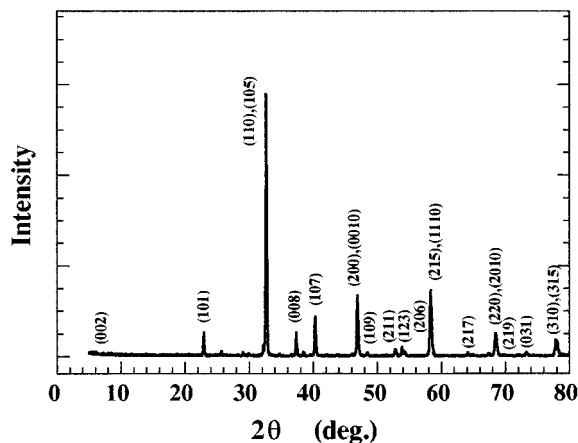


FIG. 1. X-ray diffraction pattern of a $\text{La}_{2-2x}\text{Ca}_{1+2x}\text{Mn}_2\text{O}_7$ sample ($x=0.25$).

the Mn-O-Mn exchange interaction can take place between the Mn ions in the a - b plane of the perovskite layers, whereas the exchange interaction between the double perovskite layers (in the c -axis direction) must be through O^{2-} ions. Therefore, it is likely that the physical properties of $\text{La}_{2-2x}\text{Ca}_{1+2x}\text{Mn}_2\text{O}_7$ are inherently two dimensional or quasi-two dimensional.

Resistivity ρ , MR ratio $\Delta\rho/\rho_0$, and magnetization M of $\text{La}_{2-2x}\text{Ca}_{1+2x}\text{Mn}_2\text{O}_7$ ($x=0.25$) are shown in Fig. 3 as a function of temperature. As is evident in the upper panel, the ρ - T curve at various fields exhibits a sharp cusp at ~ 96 K with semiconductor behavior above and metallic behavior below this temperature. An applied magnetic field resulted in a large reduction in resistivity. In the applied magnetic field (up to 1.8 T) examined, no saturation of magnetoresistance effect was observed. Here, it is worth noting that the materials exhibited anomalous behavior of temperature-dependent MR effects. As shown in the middle panel, the MR ratio $\Delta\rho/\rho_0$ reaches its maximum around or slightly below the cusp temperature, and $\Delta\rho/\rho_0$ at a magnetic field of $\mu_0 H=1.8$ T at

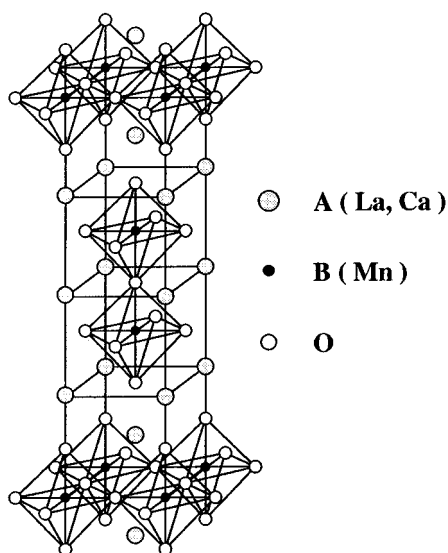


FIG. 2. Crystal structure of $\text{La}_{2-2x}\text{Ca}_{1+2x}\text{Mn}_2\text{O}_7$ with the tetragonal $\text{Sr}_3\text{Ti}_2\text{O}_7$ -type perovskite.

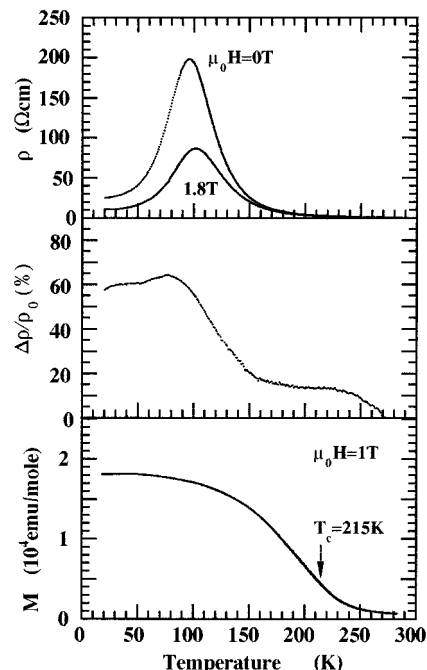


FIG. 3. Resistivity ρ , MR ratio $\Delta\rho/\rho_0$, and magnetization M of $\text{La}_{2-2x}\text{Ca}_{1+2x}\text{Mn}_2\text{O}_7$ ($x=0.25$) as a function of temperature. The resistivity ρ is measured at 0 T and 1.8 T, and magnetization M is measured at 1 T.

77 K is 64%. Even in the lower-temperature range between 20 and 77 K, large MR effects with $\Delta\rho/\rho_0$ of $\sim 60\%$ are observed. In the higher-temperature range above the cusp temperature, the MR effects decrease with increasing temperature, but still survive over a wide temperature range of up to near room temperature. The sample has a magnetic transition temperature T_c of 215 K, whose magnetic transition is shown in the bottom panel. The magnetic T_c is much higher than the cusp temperature, and is close to the temperature at which the small broad peak in MR is observed. This MR behavior is quite different from that of the ABO_3 -type materials such as $\text{La}_{1-x}\text{Ca}_x\text{MnO}$, where large MR effects are restricted to a narrow temperature range around the ferromagnetic transition. The behavior of $\text{La}_{2-2x}\text{Ca}_{1+2x}\text{Mn}_2\text{O}_7$ cannot be explained by a simple double-exchange theory.

It is well known that hole doping in ABO_3 -type perovskite manganese oxide produces metallic conductivity and ferromagnetism where the magnetic interaction is mediated by the transfer of the holes (the double-exchange interaction in the mixed $\text{Mn}^{3+}/\text{Mn}^{4+}$ valence state). With $\text{La}_{2-2x}\text{Ca}_{1+2x}\text{Mn}_2\text{O}_7$, the fundamental mechanism leading to the appearance of metallic ferromagnetism would be the same. The parent material of $\text{La}_{2-2x}\text{Ca}_{1+2x}\text{Mn}_2\text{O}_7$ is a charge transfer (CT) insulator of $\text{La}_2\text{CaMn}_2\text{O}_7$. In hole-undoped $\text{La}_2\text{CaMn}_2\text{O}_7$, the Mn^{3+} ion has the electron configuration of $t_{2g}^3 e_g^1$. Among the four 3d electrons on the Mn site, t_{2g}^3 electrons can be viewed as localized spins ($S=3/2$), while the e_g^1 electron is either itinerant or localized. Substitution of La^{3+} by Ca^{2+} introduces holes into the e_g state (some Mn^{3+} ions convert into the Mn^{4+} state without e_g^1 electrons). A sufficient amount of hole doping can lead to both ferromagnetism and metallic conductivity. We have found that hole doping with $x<0.20$ cannot produce metallic

ferromagnetism. The phase diagram as a function of temperature and nominal hole concentration x will be reported elsewhere.¹⁶

Since $\text{La}_{2-2x}\text{Ca}_{1+2x}\text{Mn}_2\text{O}_7$ with the layered perovskite structure contains two-dimensional Mn-O-Mn networks, it is reasonable to assume an anisotropic character for the magnetic and transport properties. Namely, the double-exchange interaction would be anisotropic in the a - b axis (in-plane) and c -axis (out of plane) directions. The out-of-plane component for exchange interactions should be weaker than the in-plane component. It is likely that hole transfer (electron conduction) in the out-of-plane direction is less mobile than in the a - b axis direction, which results in an increase in the out-of-plane resistivity. Similar behavior has been reported for single crystals of $\text{La}_{1-x}\text{Sr}_{1+x}\text{MnO}_4$ with two-dimensional Mn-O-Mn networks, where the motion of the doped holes appears to be highly anisotropic.¹³ Although our sample is a polycrystalline bulk, the electrical properties reflect the carrier transports for both the in-plane and out-of-plane components. In a low-temperature range around the cusp temperature the electrical properties of the materials are assumed to be dominated by less conductive transport along the out-of-plane direction, which is due to a weaker double-exchange interaction. By contrast, the magnetic transition of the bulk materials would be governed by the strong in-plane exchange interaction. Thus, the behavior of $\text{La}_{2-2x}\text{Ca}_{1+2x}\text{Mn}_2\text{O}_7$ ($x=0.25$) can be explained within the framework of the double-exchange theory by taking account of the anisotropic hole transfer and exchange interaction. To confirm this idea, further examination is necessary using single-crystal or epitaxial film samples, and such a study is currently under way.

Magnetoresistance measurements for the bulk samples of $\text{La}_{2-2x}\text{Ca}_{1+2x}\text{Mn}_2\text{O}_7$ ($x=0.25$) show a large MR effect of more than 60% of $\Delta\rho/\rho_0$ at a relatively low magnetic field of $\mu_0H=1.8$ T. This is significantly higher than that ($\Delta\rho/\rho_0<40\%$ at $\mu_0H=2$ T) reported for ABO_3 -type bulk materials such as $\text{La}_{1-x}\text{Ca}_x\text{MnO}_3$. Below the cusp temperature of 96 K (Fig. 3) there is possibly spin disorder along the out-of-plane direction, although ferromagnetic spin ordering along the in-plane direction is preserved. The application of an external magnetic field can easily increase the ferromagnetic ordering in the out-of-plane direction, leading to the pronounced MR effects observed in the low-temperature region. Moreover, it must be stressed that a very narrow one-

electron $3d$ bandwidth is expected for materials with two-dimensional Mn-O-Mn networks. It is likely that the narrow one-electron bandwidth is essential for metallic ferromagnets exhibiting large MR effects, as several authors have suggested in combination with the magnetic polaron model^{5,6} or the Kondo lattice model.⁸

In summary, we have presented results on the magnetic and electrical properties of bulk samples of layered perovskite $\text{La}_{2-2x}\text{Ca}_{1+2x}\text{Mn}_2\text{O}_7$ with two-dimensional Mn-O-Mn networks. We found that $\text{La}_{2-2x}\text{Ca}_{1+2x}\text{Mn}_2\text{O}_7$ ($x=0.25$) is a ferromagnet with $T_c=215$ K. Giant magnetoresistance (GMR) effects are observed in a wide temperature range. A striking feature of this material is that the resistivity cusp temperature is 96 K, and this is considerably lower than the magnetic transition temperature. In other words, in the ferromagnetic region both a metallic and semiconducting state exist for the $\text{La}_{2-2x}\text{Ca}_{1+2x}\text{Mn}_2\text{O}_7$ system. These phenomena could be understood by considering the effects of the anisotropic double-exchange interaction caused by the two-dimensional Mn-O-Mn networks in this material.

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