

Effect of pressure on lattice distortion, transport and magnetic properties of Pr-substituted $\text{La}_{1.2}\text{Sr}_{1.8}\text{Mn}_2\text{O}_7$ bilayered manganite

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Abstract

We have studied the effect of pressure on the anomalous lattice striction, both in the ab -plane and along the c -axis, of $(\text{La}, \text{Pr})_{1.2}\text{Sr}_{1.8}\text{Mn}_2\text{O}_7$ single crystals over the temperature region where the paramagnetic insulator to ferromagnetic metal transition takes place. We have examined the temperature dependence of the resistivity and the magnetization under applied pressure. The chemical pressure effect due to Pr-substitution at the La site suppresses the transition temperature of the parent crystal, while the application of external pressure on Pr-substituted crystals enhances the double exchange driven metallic state, resulting in a stable rise of T_c .

(Some figures in this article are in colour only in the electronic version)

1. Introduction

The observation of a phenomenon of a colossal magnetoresistance (CMR) effect has renewed the interest for doped manganites with a perovskite structure [1]. Although the insulator to metal (IM) transition and its associated CMR are well explained on the basis of the double exchange (DE) model, it was pointed out that the dynamic Jahn–Teller (JT) effect, due to the strong electron–phonon interaction, plays a significant role in the appearance of CMR as well as of the DE interaction [2, 3]. Furthermore, Dagotto *et al* proposed a phase separation model where ferromagnetic (FM) metallic and antiferromagnetic (AFM) insulating clusters coexist, which strongly supports recent experimental studies of the physics of manganites [4]. Moritomo *et al* have reported

that the $\text{La}_{1.2}\text{Sr}_{1.8}\text{Mn}_2\text{O}_7$ bilayered manganite exhibits a paramagnetic insulator (PMI) to ferromagnetic metal (FMM) transition around $T_c \sim 120$ K and an associated CMR effect [5]. The Pr(Nd)-substitution on the La site leading to $\{\text{La}_{1-z}, \text{Pr}(\text{Nd})_z\}_{1.2}\text{Sr}_{1.8}\text{Mn}_2\text{O}_7$ causes an expansion along the c -axis but a shrinkage along the $a(b)$ -axis, resulting in a change of the e_g electron occupation from the $d_{x^2-y^2}$ to the $d_{3z^2-r^2}$ orbital [6, 7]. These findings accompany not only a suppression of the PMI to FMM transition temperature, T_c , but also a variation of the easy axis of magnetization from the ab -plane to the c -axis. Application of physical pressure is a powerful tool to investigate the lattice effect on the magnetic and electronic properties of doped manganites as well as the *chemical pressure* effect due to the other rare-earth ion substitution on the La site [8]. Many studies have been carried

out so far on the effect of pressures on the structural, magnetic and transport properties in bilayered manganites [9–13].

We report here the effect of pressure on lattice striction, both in the ab -plane and along the c -axis, associated with the spontaneous PMI to FMM transition of $(\text{La}_{1-z}, \text{Pr}_z)_{1.2}\text{Sr}_{1.8}\text{Mn}_2\text{O}_7$ bilayered manganite single crystals. Ibarra *et al* have shown that, in Y-substituted $\text{La}_{2/3}\text{Ca}_{1/3}\text{MnO}_3$, a volume shrinkage of lattice in the low- T metallic state below T_c is a consequence of carrier delocalization [14]. A detailed study of anisotropic magnetoelastic effects in bilayered manganite crystals $\text{La}_{2-2x}\text{Sr}_{1+2x}\text{Mn}_2\text{O}_7$ ($0.3 \leq x \leq 0.45$) has indicated a systematic variation in the orbital state of the e_g electrons with carrier doping [15]. In addition, neutron diffraction experiments on bilayered manganites $\text{La}_{2-2x}\text{Sr}_{1+2x}\text{Mn}_2\text{O}_7$ ($0.32 \leq x \leq 0.40$) have revealed that the lattice anomalies commonly observed at T_c in CMR manganites disappear at the optimal composition of T_c , $x = 0.36$ [16]. Accordingly, the lattice distortions in CMR materials provide crucial knowledge about the role of the lattice and orbital degrees of freedom in the CMR mechanism through the Jahn–Teller-type lattice–orbital coupling.

2. Experiment

Single crystals of $(\text{La}_{1-z}, \text{Pr}_z)_{1.2}\text{Sr}_{1.8}\text{Mn}_2\text{O}_7$ ($z = 0, 0.2$ and 0.4) were grown by the floating zone method using a mirror furnace. The calculated lattice parameters of the tetragonal crystal structure of the crystals used here were shown in a previous report [7]. The dimensions of the $z = 0.2$ sample are $3.4 \times 3 \text{ mm}^2$ in the ab -plane and 1 mm along the c -axis. Measurements of thermal expansion, both in the ab -plane and along the c -axis, were done by means of a conventional strain gauge method.

Magnetostrictions and magnetoresistances were measured at the Tsukuba Magnet Laboratory, the National Institute for Materials Science (NIMS) and at the High Field Laboratory for Superconducting Materials, Institute for Materials Research, Tohoku University. Hydrostatic pressures in the lattice striction, resistivity and magnetization experiments were applied by a clamp-type cell using Fluorinert as a pressure transmitting medium. The pressure was calibrated by the critical temperature of lead. The magnetization measurements were made with a superconducting quantum interference device magnetometer, both at Iwate University and NIMS.

3. Results and discussion

First of all, in figure 1(a), we present the temperature variation of the ab -plane resistivity of the Pr-substituted $z = 0.2$ crystal under applied pressures of 0, 0.5 and 0.8 GPa. For comparison, the resistivity data for the same crystal are given in a magnetic field of 8 T ($H \parallel ab$). The applied pressure enhances the PMI to FMM transition temperature T_c from $\sim 90 \text{ K}$ at 0 GPa up to $\sim 105 \text{ K}$ at 0.8 GPa, and reduces the resistivity values over the whole measured temperature range. The value of T_c increases with pressure as $dT_c/dP = 18.8 \text{ K GPa}^{-1}$, which is the same as the pressure dependence of the transition temperature, $dT_c/dP = 19 \text{ K GPa}^{-1}$, for the parent crystal [11]. Figure 1(b)

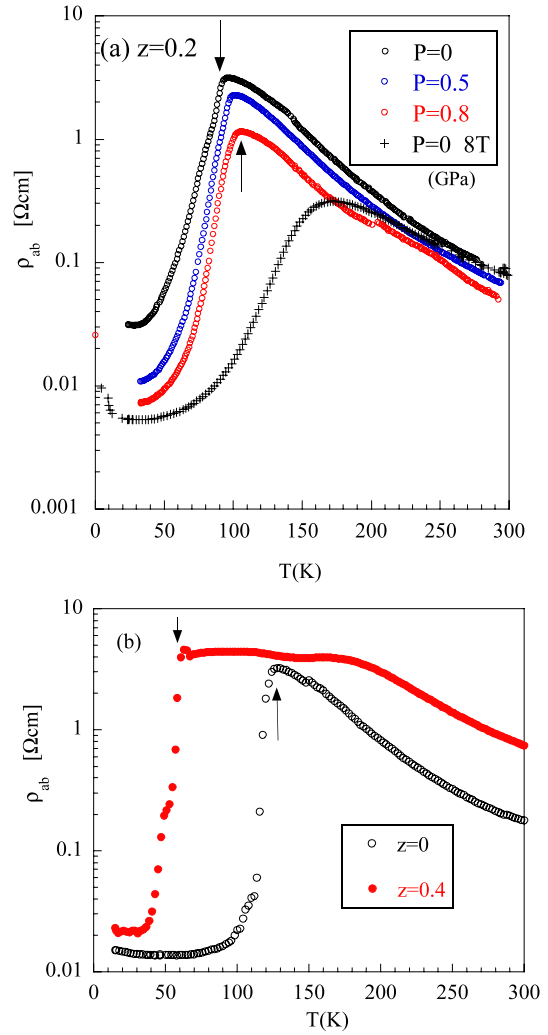


Figure 1. (a) Temperature variation of the ab -plane resistivity of the Pr-substituted $z = 0.2$ crystal under applied pressures of 0, 0.5 and 0.8 GPa. For comparison, the resistivity data are given in a magnetic field of 8 T ($H \parallel ab$). (b) ab -plane resistivity of the parent and $z = 0.4$ crystals as a function of temperature without applied pressure. Arrows denote the insulator to metal transition temperatures at ambient pressure, which almost agree with the Curie temperatures.

denotes the ab -plane resistivity of the parent and $z = 0.4$ crystals as a function of temperature without applied pressure. The Pr-substitution for the La site strongly degrades T_c from 120 K at $z = 0$ (parent) down to 60 K at $z = 0.4$ through 90 K at $z = 0.2$.

Next, let us show in figure 2, the effect of pressure on the ab -plane magnetization of the $z = 0.2$ and 0.4 crystals. For $z = 0.2$, the value of magnetization at low temperatures under 1 T reaches $\sim 70 \text{ emu g}^{-1}$, close to the fully ferromagnetic moment of $3.6 \mu_B/\text{Mn}$ site. The pressure dependence of T_c at $z = 0.2$ is estimated to be $\sim 17 \text{ K GPa}^{-1}$ from the magnetization data, which is in good agreement with the T_c variation with pressure from the resistivity data. For $z = 0.4$, weak ferromagnetism appears below $\sim 60 \text{ K}$, where the value of ρ reaches its maximum value. From both figures 1(b) and 2(b), we notice a slope change in the resistivity curve of

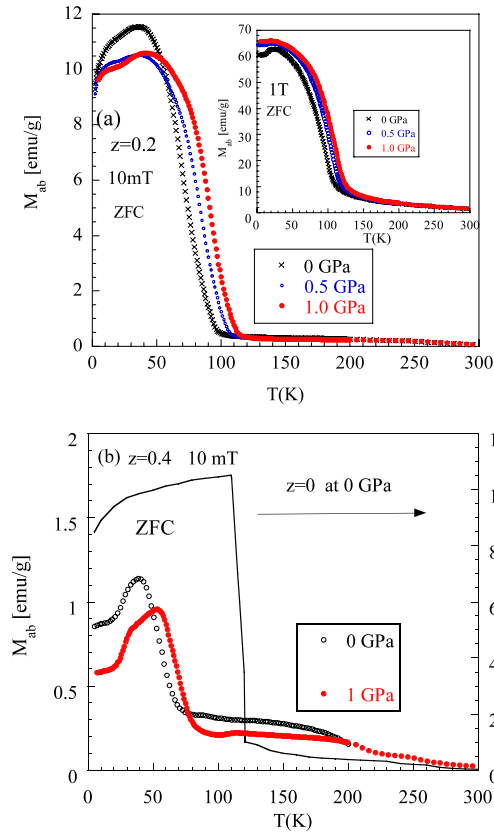


Figure 2. Effect of pressure on the zero field cooled (ZFC) ab -plane magnetization M_{ab} . (a) The $z = 0.2$ crystal under 0, 0.5 and 1.0 GPa in an applied field of 10 mT. The inset shows M_{ab} data of the $z = 0.2$ crystal in 1 T. (b) The $z = 0.4$ crystal under 0 and 1.0 GPa in 10 mT. For comparison, the M_{ab} data of $z = 0$ crystal at ambient pressure are displayed.

the $z = 0.4$ crystal at around 200 K and its associated magnetic anomaly in the magnetization curve at the same temperature. This peculiar behavior probably indicates that FMM clusters of a pseudocubic phase such as $(La_{0.6}, Pr_{0.4})_{1-x}Sr_xMnO_3$ with high T_c are dispersed within the double layered matrix, although the x-ray diffraction analysis on all samples including the $z = 0.4$ crystal never detected such impurity phase.

Now, we examine the effect of pressure on the lattice striction, both in the ab -plane and along the c -axis, accompanied by the spontaneous PMI to FMM transition, as shown in figures 3(b) and (c). We note that $dL = L(T) - L(200 \text{ K})$ at 0 T. For the $z = 0.2$ crystal, the value of $dL_c(T)/L_c(200 \text{ K})$ shows a sizable decrease around T_c at both ambient pressure and an external pressure of 0.8 GPa with decreasing temperature, while the ab -plane lattice striction exhibits no prominent anomaly near T_c . Here, the variations of the c -axis lattice parameters associated with the PMI to FMM transition are estimated to be $\Delta c/c \sim -0.04\%$ and -0.07% , for 0 and 0.8 GPa, respectively, which agree well with the c -axis magnetostriction near T_c . The lattice shrinkage due to the application of magnetic field is closely related to the CMR effect in doped manganese oxides.

On the other hand, the ambient lattice striction of the parent crystal near T_c expands along the c -axis but shrinks in

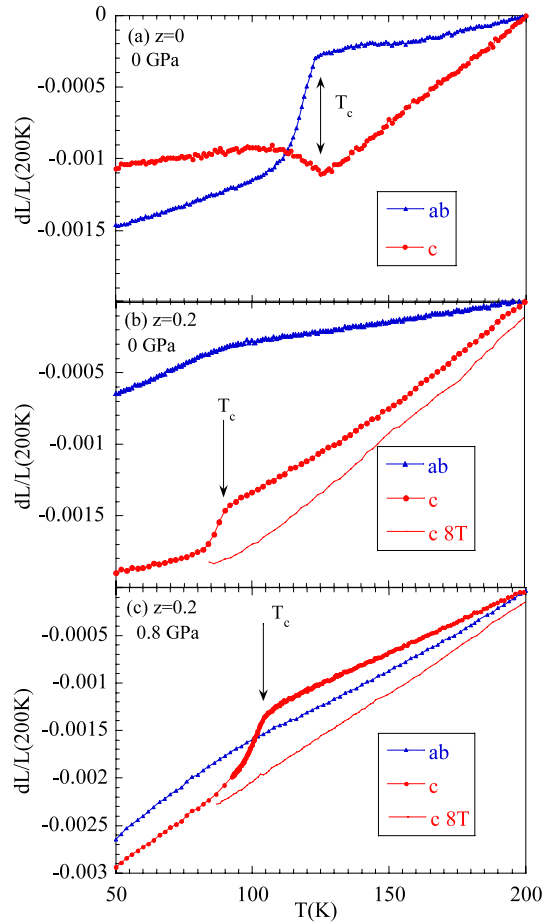


Figure 3. The effect of pressure on the lattice striction, both in the ab -plane and along the c -axis, associated with the spontaneous PMI to FMM transition. (a) $z = 0$. (b) $z = 0.2$ at ambient pressure. (c) $z = 0.2$ at an applied pressure of 0.8 GPa. The $dL_c(T)/L_c(200 \text{ K})$ data are also shown at an applied field of 8 T under ambient pressure and 0.8 GPa. ($H \parallel ab$).

the ab -plane (see figure 3(a)). The qualitative difference in the anisotropic lattice anomalies between the $z = 0.2$ and parent crystals is reduced to a change of the e_g electron occupation between the $d_{x^2-y^2}$ and the $d_{3z^2-r^2}$ orbital [6, 7]. In the PMI state above T_c , we assume that the local lattice distortion of MnO_6 octahedron strongly couples with the orbital state of the e_g electron through the local JT effect. Upon decreasing T across T_c , the lattice distortion is relaxed due to the itinerant state of carriers, resulting in the observed lattice anomalies. For the parent crystal, we expect from the large decrease in $\Delta a/a \sim -0.08\%$ near T_c that the $d_{x^2-y^2}$ orbital state is dominant. Contrary to it, for the Pr-substitution crystal, the rapid shrinkage of $dL_c(T)/L_c(200 \text{ K})$ gives rise to the $d_{3z^2-r^2}$ orbital state being elongated along the c -axis in the PMI phase.

Furthermore, figure 4 represents the ab -plane and the c -axis thermal expansion data of the $z = 0.4$ crystal with $T_c \sim 60 \text{ K}$ (ambient pressure). We notice a qualitative difference in the ab -plane lattice striction between 0 and 0.8 GPa. The ambient value of $dL_{ab}(T)/L_{ab}(200 \text{ K})$ shows no visible change around T_c , but the high-pressure data exhibit a clear upturn in the ab -plane below T_c accompanied by an

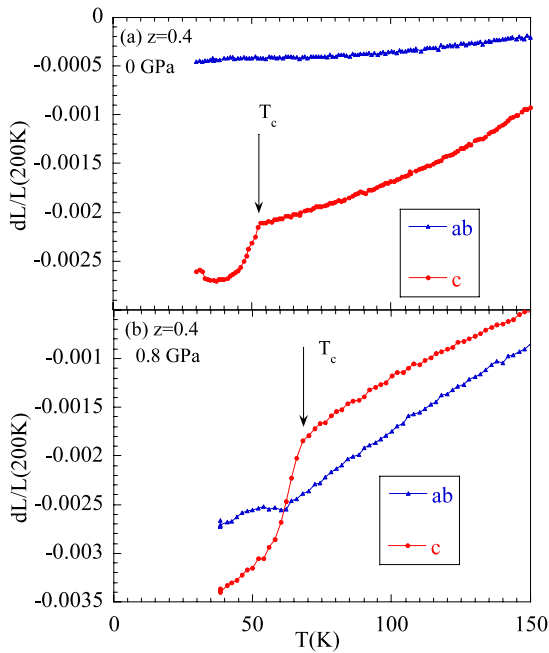


Figure 4. The effect of pressure on the lattice striction, both in the *ab*-plane and along the *c*-axis, associated with the spontaneous PMI to FMM transition. (a) $z = 0.4$ at ambient pressure. (b) $z = 0.4$ at an applied pressure of 0.8 GPa.

enhanced lattice shrinkage along the *c*-axis, $\Delta c/c \sim -0.11\%$ (-0.07% at 0 GPa). These findings contrast with a substantial upturn in $dL_c(T)/L_c(200\text{ K})$ below $T_c \sim 120\text{ K}$ (ambient pressure) for the $z = 0$ parent crystal.

We comment now on the pressure effect on the MnO_6 octahedron in the parent bilayered manganite $\text{La}_{1.2}\text{Sr}_{1.8}\text{Mn}_2\text{O}_7$. Argyriou *et al* have reported that upon increasing the pressure up to 0.6 GPa, in the PMI phase, both the Mn–O(1) and Mn–O(3) bond lengths shrink but the Mn–O(2) bond length elongates [9]. Here, the O(1) and O(2) oxygen atoms are located at the apical site along the *c*-axis, where O(1) lies between two MnO_2 layers and O(2) within a rocksalt-type La/Sr–O layer. The O(3) oxygen atom is within the MnO_2 layer. Assuming such a variation of the MnO_6 octahedron in the PMI state of Pr-substituted $\text{La}_{1.2}\text{Sr}_{1.8}\text{Mn}_2\text{O}_7$, the Mn–O(1)–Mn interactions along the *c*-axis and the Mn–O(3)–Mn interactions in the *ab*-plane are expected to be strengthened upon application of pressure. In other words, the double exchange (DE) interaction between Mn^{3+} and Mn^{4+} within the MnO_2 single layer and the DE interaction along the *c*-axis within the bilayer are enhanced; this is closely related to a rise of T_c with pressure. On the other hand, for the Pr-substituted crystal, the Mn–O(1) bond length is elongated upon increasing Pr, reducing the transfer integral between Mn–O(1)–Mn within the bilayer [17]. As a result, the FMM phase is suppressed at heavy Pr-substitution. Accordingly, it is concluded from the microscopic measurements on both external and chemical pressure effects that the effect of pressure on Pr-substituted crystals causes a reduction of the elongated Mn–O(1) bond length accompanied by an expansion of the Mn–O(2) bond length, resulting in a stable rise of T_c . These findings are consistent with our data of lattice distortion.

4. Summary

We have studied the effect of pressure on the unusual lattice striction, both in the *ab*-plane and along the *c*-axis, of $(\text{La, Pr})_{1.2}\text{Sr}_{1.8}\text{Mn}_2\text{O}_7$ bilayered manganite single crystals. We have also examined the temperature dependence of the resistivity and the magnetization under applied pressure. The pressure coefficient, dT_c/dP , for the $z = 0.2$ crystal is estimated to be $\sim 19\text{ K GPa}^{-1}$ from the transport and magnetic properties, which is in good agreement with that of the parent material. The chemical pressure effect due to Pr-substitution at the La site suppresses the PMI–FMM transition temperature of the Pr-free crystal. However, the application of hydrostatic pressure on the Pr-substituted crystal enhances the double exchange driven FMM state, resulting in a stable rise of T_c . The pressure effect on lattice distortion near T_c gives rise to a larger shrinkage of the *c*-axis by $\Delta c/c \sim -0.07\%$ and -0.11% at $z = 0.2$ and 0.4 , respectively. The *c*-axis lattice shrinkage enhanced below T_c indicates that the MnO_6 octahedron couples with the $d_{3z^2-r^2}$ orbital state in the PMI state. Our data are well explained on the basis of both the external and chemical pressure effects on the MnO_6 octahedron in bilayered manganites [9, 17].

Acknowledgments

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