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Pressure Effect on Electrical Properties of a Manganate with Nominal Composition $La_{1.0}Ca_{2.0}Mn_2O_7$ *

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Abstract: Pressure effects on electrical properties of a manganate with nominal composition $La_{1.0}Ca_{2.0}Mn_2O_7$, which has a layered perovskite structure as majority phase, have been investigated under hydrostatic pressures up to 1.05 GPa by using a self-clamped CuBe piston-cylinder cell. An abnormal pressure effect was observed. At a pressure of 0.55 GPa, a large pressure resistance effect of ≈40% was observed in a lower temperature range of 5～150 K. Besides, it is found that the metal-insulator transition temperature increases at low pressure but deceases with further loading pressure.

Key words: layered perovskite manganate; electrical resistivity; pressure resistance effect

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1 Introduction

The layered manganate $(R_{1-x}A_x)_{n+1}Mn_nO_{3n+1}$ (R is a rare-earth ion and A is a divalent cation, n=1,2,3) has become a research subject of intense interest[1-4]. Their layered crystallographic structure provides an anisotropic and low-dimensionality character. It is well known that electron correlations are enhanced in low-dimensional materials. Hence, the magnetotransport phenomena for these compounds are expected to be interesting in terms of anisotropic transport and exchange interactions. Kimura et al. reported the anisotropy in resistivity in $La_{1.4}Sr_{1.6}Mn_2O_7$ single crystal and observed that the resistivity along c-direction (ρ_c) is larger than that in-plane (ρ_{ab}) by a factor of 10^3 at room temperature. Meanwhile it was reported that $La_{1.4}Sr_{1.6}Mn_2O_7$ single crystal shows magnetoresistance (MR) effect of 80% at a field of 0.3 T[4].

The pressure, as a thermodynamic variable, has been used as a powerful probe for investigation of the three-dimensional perovskite manganates[5-8]. These experiments show that high pressure has substantial effects on electrical transport properties and the metal-insulator transition temperature (T_{MI}) in those manganates. The decrease of electrical resistance and the increase of T_{MI} with increasing pressure are intimately associated with pressure-induced reduction of Jahn-Teller distortion and possible enhancement of the double-exchange interaction. The transport and magnetic properties of layered manganates are also very sensitive to applied pressures due to the anisotropic compressibility of these

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materials. Mahesh et al. reported that the layered manganates $La_{2-2x}Sr_{1+2x}Mn_2O_7$ show significant difference in their electronic behavior on the application of pressure compared to three-dimensional (3D) perovskites. The dT_{MI}/dp of the layered manganates $La_{2-2x}Sr_{1+2x}Mn_2O_7$ is about 5 K · GPa^{-1}, while that of 3D perovskite manganates is as high as 36 K · GPa^{-1}. Also, the depression rate in MR by pressure for 3D perovskite manganates is higher than that observed in layered manganates $La_{2-2x}Sr_{1+2x}Mn_2O_7$[9]. Kimura et al. studied the external pressure effect on magnetic and transport properties of the $La_{1.4}Sr_{1.6}Mn_2O_7$ and reported that the applied pressure weakens the inter-plane magnetic coupling[10]. Argyriou et al. reported that the layered manganate $La_{2-2x}Sr_{1+2x}Mn_2O_7$ shows remarkable difference in their electronic transport behavior under pressure compared to the isotropic 3D perovskite counterparts. Different from the case in the 3D perovskite, the two-dimensional structure appears to accommodate the pressure effects through the change in Mn—O bond lengths rather than by the tilting of the MnO_6 octahedral[11]. The existing reports about the effect of hydrostatic pressure on the structure and properties for layered manganates are focused on the $La_{2-2x}Sr_{1+2x}Mn_2O_7$ series, while the $La_{2-2x}Ca_{1+2x}Mn_2O_7$ series has not been received considerable attention.

Kamenev et al. studied the transport properties of layered perovskite $La_{1.2}Ca_{1.8}Mn_2O_7$ under pressure and found that the applied pressure reduces the electrical resistivity and the Curie temperature increases with applied pressure at a rate of 11 K · GPa^{-1}[12]. However, there are some arguments about the synthesis, structure and properties of the manganates $La_{2-2x}Ca_{1+2x}Mn_2O_7$ reported in literatures. Asano et al. reported firstly that the layered perovskite manganates $La_{2-2x}Ca_{1+2x}Mn_2O_7$ can be synthesized in the range of $0 \leqslant x \leqslant 0.5$ and the system shows a metallic ferromagnetic state accompanying with colossal magnetoresistance (CMR) effect in the range of $0.22 \leqslant x \leqslant 0.5$[13]. Later, Ganguly et al.[14] and Zhu et al.[15] studied the same nominal composition sample ($x=0.25$) that Asano et al. mentioned and found that the sample does not form layered perovskite-like manganate. The observed physical properties of the manganate arise mainly from multiphase including hole-doped 3D perovskite manganate. Recently, Fawcett et al. synthesized the electron-doped layered perovskite manganates $La_{2-2x}Ca_{1+2x}Mn_2O_7$ ($0.6 \leqslant x \leqslant 1.0$) by using a citrate gel process and observed that all samples exhibit insulating behavior without CMR effect due to charge ordering in the temperature range of 5 ~ 300 K[16].

We have carried out studies on the structure and physical properties of the manganate with nominal composition $La_{1.0}Ca_{2.0}Mn_2O_7$[17]. The results show that it is very difficult to form a pure layered perovskite $La_{1.0}Ca_{2.0}Mn_2O_7$. Instead, it forms multiphase mixtures comprising the layered perovskite mangante $La_{1.0}Ca_{2.0}Mn_2O_7$ as a majority and a small amount of perovskite mangante $La_{0.5}Ca_{0.5}MnO_3$ as a minority. A considerable magnetoresistance (MR) effect was observed for the sample, which is mainly from the layered perovskite mangante, in lower temperature range. Therefore, it is very interesting to study the pressure effects on the transport properties of this sample.

2 Experiment

The synthesis, structural determinations and properties of $La_{1.0}Ca_{2.0}Mn_2O_7$ have been described previously[17]. The sample with nominal composition $La_{1.0}Ca_{2.0}Mn_2O_7$ was prepared by standard solid-state reaction method. The structure of the sample was investigated using powder X-ray diffraction, Rietveld analysis and TEM experiments.

The resistivity of the sample was measured using a standard four-probe method. Temperature dependence of the electrical resistance under hydrostatic pressure up to 1.05 GPa was measured using a self-clamped CuBe piston-cylinder cell. The sample size is 5 mm × 2 mm × 0.5 mm. The kerosene-sili-

con oil (1 ∶ 1) was used as pressure-transmitting medium. The pressure was first loaded at room temperature and then screw-locked. The pressure was calibrated utilizing a manganin gauge and the temperature was monitored using a chromel-alumel thermocouple placed near the sample. The pressure resistance (PR) ratio is defined here as $-\Delta R/R_0=-(R_p-R_0)/R_0$, where R_0 and R_p denote resistences at ambient pressure and an applied pressure, respectively.

3 Results and Discussion

Our synthesized sample is a multiphase mixture comprising the layered perovskite manganate $La_{1.0}Ca_{2.0}Mn_2O_7$ with 91.3% mass fraction as a majority phase and the perovskite manganate $La_{0.5}Ca_{0.5}MnO_3$ with mass fraction 8.7% as a minority phase. X-ray diffraction pattern of the sample is presented in Fig. 1 and refined parameters are listed in Table 1.

Table 1 Structural Parameters obtained from Rietveld refinement of the room temperature X-ray data for the sample with nominal composition $La_{1.0}Ca_{2.0}Mn_2O_7$

Phase	Atom	Wyck[a]	SOF[b]	x	y	z	B/(nm^2)
$La_{1.0}Ca_{2.0}Mn_2O_7$ a=0.383 54(3) nm c=1.926 79(7) nm Space group: $I4/mmm$ Mass fraction: 91.3%	Ca(P)	2b	0.2	0.000 0	0.000 0	0.500 0	0.000 1
	La(P)	2b	0.8	0.000 0	0.000 0	0.500 0	0.000 1
	Ca(R)	4e	0.8	0.000 0	0.000 0	0.309 0(7)	0.000 1
	La(R)	4e	0.2	0.000 0	0.000 0	0.309 0(7)	0.000 1
	Mn	4e	1.0	0.000 0	0.000 0	0.095 7(2)	0.000 1
	O(1)	2a	1.0	0.000 0	0.000 0	0.000 0	0.000 1
	O(2)	8g	1.0	0.000 0	0.500 0	0.093 1(9)	0.000 1
	O(3)	4e	1.0	0.000 0	0.000 0	0.191 9(5)	0.000 1
	$l_{Mn-O(1)}$=0.184 35(2)(nm), $l_{Mn-O(2)\times4}$=0.191 98(1)(nm), $l_{Mn-O(3)}$=0.185 31(8)(nm)						
	$\theta_{Mn-O(2)-Mn}$=177.9(1)°, $\theta_{Mn-O(1)-Mn}$=180.0°						
Phase	Atom	Wyck[a]	SOF[b]	x	y	z	B/(nm^2)
$La_{0.5}Ca_{0.5}MnO_3$ a=0.541 64(5) nm b=0.544 54(7) nm c=0.770 99(8) nm Space group: $Pbnm$ Mass fraction: 8.7%	Ca	4c	0.4	0.506 0(2)	0.519 0(4)	0.250 0	0.000 1
	La	4c	0.6	0.506 0(2)	0.519 0(4)	0.250 0	0.000 1
	Mn	4b	1.0	0.500 0	0.000 0	0.000 0	0.000 1
	O(1)	4c	1.0	0.444 1(3)	1.000 0	0.250 0	0.000 1
	O(2)	4d	1.0	0.746 4(5)	0.294 4(6)	0.024 3(7)	0.000 1
	$l_{Mn-O(1)}$=0.151 2(3) nm, $l_{Mn-O(2)}$=0.209 11(4) nm						
	$\theta_{Mn-O(2)-Mn}$=164.4°, $\theta_{Mn-O(1)-Mn}$=162.5°						

Note: (a) Multiplicity and Wyckoff notation; (b) Occupancy. R_p=6.24, R_{wp}= 12.43.

Electrical resistivity (ρ) versus temperature for the sample at different pressures are shown in Fig. 2. At ambient pressure (p=0 GPa), the sample shows a sharp peak in the resistivity vs. temperature relationship corresponding to metal-to-insulator transition (T_{MI}) at 110 K. It exhibits insulating behavior (i. e. a negative dρ/dT) above T_{MI} and metallic behavior (a positive dρ/dT) below T_{MI}. Below T_{MI}, ρ decreases slowly in the temperature range of 100～50 K and then increases slowly below 24 K. The insulator behavior below 24 K might be linked to a low temperature localization effect.

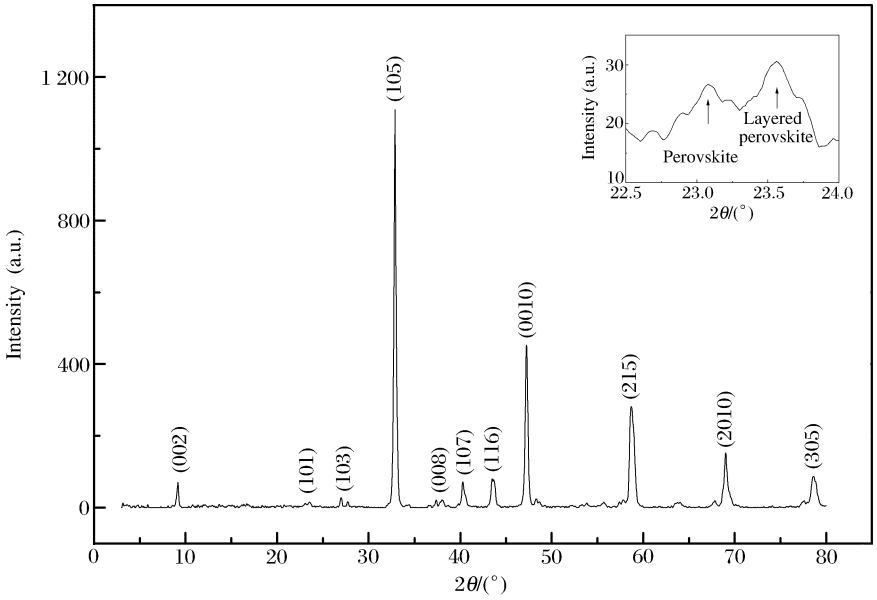


Fig. 1　X-ray diffraction pattern of the sample with nominal composition $La_{1.0}Ca_{2.0}Mn_2O_7$ (The inset shows the enlarged X-ray diffraction pattern in the range of 22.5°～24°)

The application of pressure leads to a decrease in ρ. One possibility is that the grain boundaries are compressed in the sample and the conductivity is enhanced due to the compact sample under pressure. The pressure effect on the crystal structure and the enhancement of conductivity will be discussed later. With increasing pressure, the maximum position of $\rho(T)$ shifts to a slightly higher temperature in the pressure range of 0 ～ 0.55 GPa. The dT_{MI}/dp of the sample is about 14 K · GPa^{-1} in the pressure range of 0 ～ 0.55 GPa. This value is smaller than that of the 3D perovskite manganates (36 K · GPa^{-1}), and close to that of layered perovskite $La_{1.2}Ca_{1.8}Mn_2O_7$ (11 K · GPa^{-1}). Though the ratio of the $La_{1.0}Ca_{2.0}Mn_2O_7$ and $La_{0.5}Ca_{0.5}MnO_3$ was determined through X-ray diffraction analysis, it is still difficult to analyze the corresponding physical properties quantitatively.

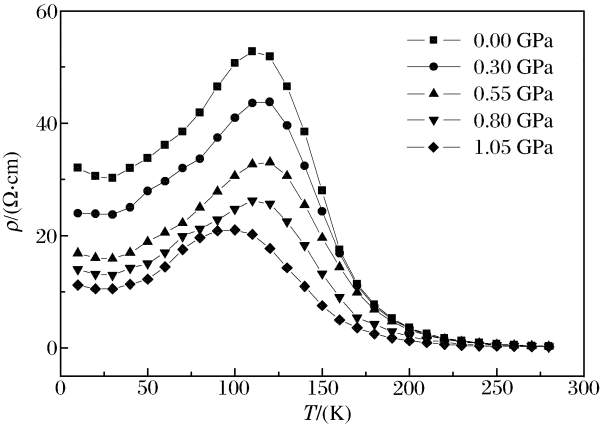


Fig. 2　The temperature dependence of the electrical resistivity of the sample with nominal composition $La_{1.0}Ca_{2.0}Mn_2O_7$ at different pressures

In a sense, magnetic field and pressure seem to have similar effects: they both reduce the resistance and shift T_{MI} to higher temperatures. Below T_{MI}, electronic transport is predominantly controlled by the transfer integral $t_{eff} = t_0\cos(\theta/2)$. The pressure affects the one-electron bandwidth ($\propto t_0$) whereas the magnetic field affects the angle θ between the t_{2g} spins. Enhancement in t_0 or decrease in θ (θ tends to zero in the ferromagnetic state) will increase t_{eff} and thus give rise to decrease in resistivity. As shown in Fig. 3(a), at a pressure of 0.55 GPa, a large PR effect of ≈40% is observed in the temperature range of 5～150 K. Above 150 K, the PR effect decreases quickly with increasing temperature. Similarly, as shown in Fig. 3(b), at a magnetic field of 4 T, there is a large MR effect of ≈65%

in the temperature range of 5～150 K on the manganate with nominal composition $La_{1.0}Ca_{2.0}Mn_2O_7$. It has been explained that the MR effect in the lower temperature arises from the layered perovskite majority phase[17]. Thus, it is reasonable to deduce that the PR effect in the lower temperature range also arises mainly from the layered perovskite majority phase.

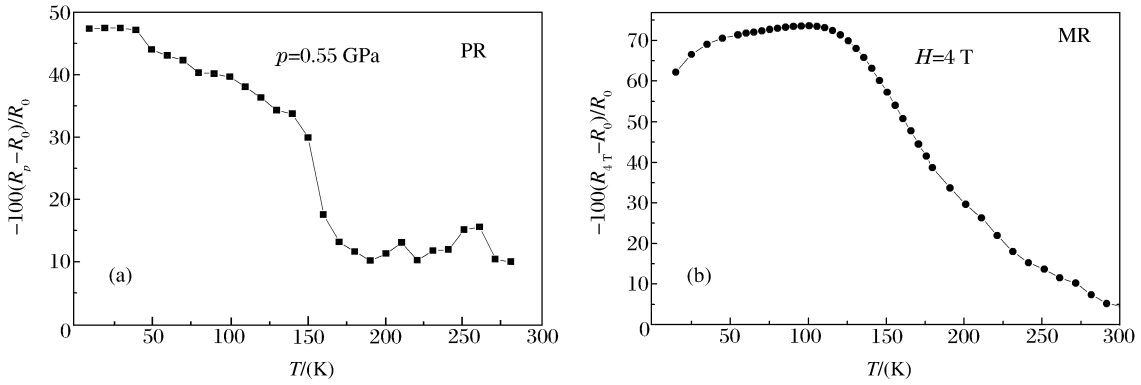


Fig. 3 The pressure resistance effect at 0.55 GPa (a), and magnetoresistance effect at a magnetic field of 4 T (b) versus temperature of the sample with nominal composition $La_{1.0}Ca_{2.0}Mn_2O_7$

The applied pressure affects mainly the interbilayer spacing and brings rigid bilayers closer to each other, and leads to an increase in the transition temperature. This indicates that the application of pressure normally favors the ferromagnetic metal phase and suppresses the interplane magnetic and charge couplings. The increase in the transition temperature can be interpreted as a consequence of increased electronic hopping under pressures, which is caused by the increased overlap between adjacent orbitals under high pressure. According to the double exchange theory[18-20], high pressure increases the delocalization of the electrons and favors the ferromagnetic coupling in the structure, and results in the decrease in resistance and the increase in T_{MI}.

The T_{MI} of the sample versus pressure is shown in Fig. 4. The T_{MI} increases from 110～118 K with increasing pressure from ambient to 0.55 GPa and the coefficient of dT_{MI}/dp is positive. However, with increasing pressure further, the dT_{MI}/dp changes to negative value. This phenomenon is different from the pressure effect on $La_{2-2x}Sr_{1+2x}Mn_2O_7$ series compound, ABO_3-type compound and layered perovskite $La_{1.2}Ca_{1.8}Mn_2O_7$ mentioned in the introduction. In Fig. 2, it can be seen that the metal-insulator transition peak becomes broader with increasing pressure, especially above 0.55 GPa. It is known that the crystal structure of the layered perovskite manganate $Ca_3Mn_2O_7$ is unstable under high pressure[21] or by La-doping[22], and transforms to an orthorhombic structure from the tetragonal structure at about 1.6 GPa. One possibility is that the crystal structure of $La_{1.0}Ca_{2.0}Mn_2O_7$ is also unstable under pressure and occurs the phase transition at lower pressure than $Ca_3Mn_2O_7$ (but above 0.55 GPa) due to La-doping. In the pressure range of 0～0.55 GPa, the crystal structure is still kept the same and high pressure increases the one-electron bandwidth as well as decreases the θ close to 0°, thus the T_{MI} increases with

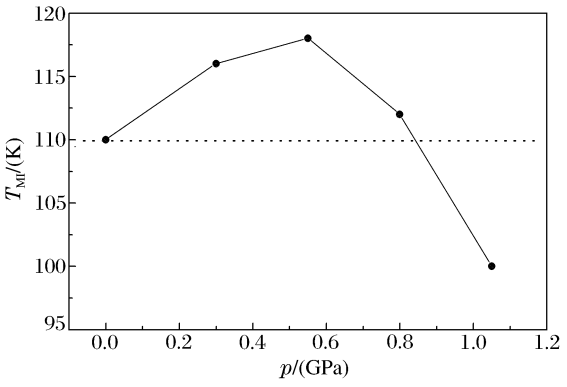


Fig. 4 The T_{MI} of the sample with nominal composition $La_{1.0}Ca_{2.0}Mn_2O_7$ versus pressure

increasing pressure as other manganates do. But above 0.55 GPa, the crystal structure might start to transform and the MnO_6 octahedral might be distorted and tilted due to the transformation to a low symmetry structure, thus the θ becomes far away from 0° and the transfer integral reduces. This case will result in the decrease of T_{MI} with pressure. Above analysis is not a definite but a possible expression. There are still many uncertainties. Further studies are eager to be carried out.

4 Conclusions

We have studied the pressure effects on electrical properties of the manganate with nominal composition $La_{1.0}Ca_{2.0}Mn_2O_7$. Its metal-insulator transition temperature T_{MI} is about 110 K at ambient pressure. The electrical resistivity is strongly reduced under pressure and the dT_{MI}/dp of the sample is about 14 K · GPa^{-1} in the pressure range of 0～0.55 GPa. There is a large PR effect in the low temperature range of 5～150 K, which arises mainly from the layered perovskite majority phase. T_{MI} increases with pressure in the pressure range of 0～0.55 GPa while decreases in the pressure range of 0.55～1.05 GPa.

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名义成分为 $La_{1.0}Ca_{2.0}Mn_2O_7$ 锰氧化物的压阻效应

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摘要：利用低温高压电阻原位测量装置（自箝铍青铜活塞-圆筒式压砧），在 0～1.05 GPa 静水压力范围内，对以层状钙钛矿结构为主相、名义成分为 $La_{1.0}Ca_{2.0}Mn_2O_7$ 的锰氧化物样品进行了压阻效应研究。实验观测到异常的压阻效应。在低温 5～150 K 范围内，压力为 0.55 GPa时，样品呈现出高达 40％的压阻效应，而且，金属-绝缘体相变温度在低压范围内随压力的增加而增加，但随着压力的进一步增加而减小。

关键词：层状钙钛矿结构锰氧化物；电阻率；压阻效应

中图分类号：O521.2 **文献标识码**：A