STRUCTURE AND MAGNETORESISTANCE OF
Pr$_{0.7}$(Sr$_{0.3-y}$Ca$_y$)MnO$_3$*

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We have investigated the structural and magnetoresistive properties for a series of Pr$_{0.7}$(Sr$_{0.3-y}$Ca$_y$)MnO$_3$ with $y = 0$ to 0.3. A systematic decrease in a- and c-lattice parameter was observed, while b-lattice parameter remains as a constant with $y$ increasing from 0 to 0.3. A significant reduction in the planar Mn-O-Mn bond angle is accompanied by an enhancement of magnetoresistance. Our results can be explained based on the model of spin-disorder scattering, in which the electronic bandwidth plays an important role on determining the relation between resistivity and magnetization.

1. Introduction

The observation of Colossal Magnetoresistance (CMR) near Curie temperature in the perovskites (R$_{1-x}$A$_x$)MnO$_{3-\delta}$ ("A" denotes a divalent alkaline-earth ion, and R is a trivalent rare-earth element) has attracted much attention to both academic and industrial communities. From the aspect of applications, the magnetic field induced change in resistance (>99%) is nearly two orders of magnitude higher than that of a conventional magnetoresistance (MR) material, and, hence, the sensitivity of a sensor based on the MR effect can be improved dramatically. However, the challenge remains for the applications purposes, owing to the low Curie temperature $T_c$ and the high saturation field of these oxide compounds. But, on the other hand, the mechanism of CMR is an interesting topic to explore, even it is not yet fully understood. Many models have been proposed to account for the origin of CMR, including the scattering of electrons by polaron, an increase of hopping integral between Mn-ion, Jahn–Teller effect, and others. Although these models have not been unified at this stage, several important factors affecting the value of CMR have been pointed out consistently: ratio of Mn$^{+4}$/Mn$^{+3}$, effective radius of an A or R atom, Curie temperature $T_c$, Mn-O bond length, and the bond angle of Mn-O-Mn. In the conventional double exchange (DE) mechanism for explaining

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the transport and magnetic properties of (La$_{1-x}$A$_x$)MnO$_3$, the electronic conductivity ($\sigma$) is directly related to its ferromagnetism via the DE mechanism between the parallel spins of neighboring Mn-ions through the O-ion. Zener et al.\(^8\) described this mechanism by a simple expression: $\sigma = (x e^2 / a h)(T_c / T)$, where $e$ is the electronic charge, $h$ the Plank constant and $a$ the lattice parameter associated with the cubic structure of (La$_{1-x}$A$_x$)MnO$_3$. Based on this formula, the mixed states of +4 and +3 for the Mn-ions play a crucial role to induce the paramagnetic insulator–ferromagnetic metal transition, resulting in an appreciable electronic conductivity. Later, it was pointed out by de Gennes\(^9\) in 1959 that the true double exchange situation exists only when $b \ll J_i S$, where $b$ is the hopping integral, $S$ the total spin moment, and $J_i$ the intra-atomic exchange coupling. Namely, if the kinetic energy of the spin is comparable to the exchange energy, a complicated relation may occur between conductivity and magnetic behavior. Since the strength of $J_i$ and $b$ strongly depend on the Mn-O bond-length, and the Mn-O-Mn bond angle, the full understanding of the CMR effect must rely on a detailed study on the correlation between the local Mn-O-Mn structure, and the magnetoresistive behavior. In an attempt to seek such information, we study the properties of resistivity, magnetization and the local Mn-O-Mn structure on a series of bulk samples, Pr$_{0.7}$Sr$_{0.3-y}$Ca$_y$MnO$_3$. This series of compounds was chosen because of the following advantages: (1) a wide range of $T_c$ by adjusting the Ca content from 0 to 0.3, (2) the ratio of Mn$^{+4}$/Mn$^{+3}$ is not changed upon replacing Sr$^{+2}$ by a smaller Ca$^{+2}$, and (3) an extra-high CMR value has been observed at $y = 0.3$.\(^10\)

2. Experimental

The polycrystalline Pr$_{0.7}$Sr$_{0.3-y}$Ca$_y$MnO$_3$ samples with $y = 0$ to 0.3 were prepared by the standard solid-state reaction method. High purity of Pr$_6$O$_{11}$, CaO, SrO$_3$, and MnO$_2$ powders were mixed and calcinated at 850°C for 12 hours, then, sintered at 1500°C for another 12 hours. The repeating of powder-grinding in the process of sintering improved the phase-purification of samples. The X-ray diffraction analyses carried out with a Scientag (X1) diffractometer (CuK$\alpha$ radiation). Rietveld refinement of the XRD data were performed using the GSAS package.\(^11\) The valence of Mn was determined by the X-ray absorption technique as described in Ref. 12. Bar-shaped samples of $6 \times 2 \times 1$ mm$^3$ were cut out from the sintered pellets to be used for the standard four-point resistivity measurement with magnetic field changing from zero to 1.6 tesla. The Curie temperatures of the samples were determined from the magnetization versus Temperature (M–T) curves which were measured at 1000 Gauss, using a commercial SQUID (Quantum Design) magnetometer.

3. Results and Discussion

Based on the analysis of x-ray absorption spectra, the valence of Mn-ion is 3.56±0.05 for all measured samples. $T_c$ was determined from the M–T curve, as the onset temperature from the paramagnetic to ferromagnetic phase. They are 310, 280, 140, 138,
Table 1. The structural parameters for Pr$_{0.7}$Sr$_{0.3-y}$Ca$_y$MnO$_3$.

<table>
<thead>
<tr>
<th>y</th>
<th>a</th>
<th>b</th>
<th>c</th>
<th>Mn-O (Apical)</th>
<th>Mn-O (Planar)</th>
<th>Mn-O-Mn (Apical)</th>
<th>Mn-O-Mn (Planar)</th>
<th>wRp</th>
<th>Rp</th>
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<tr>
<td>0</td>
<td>5.4743(7)</td>
<td>5.4705(7)</td>
<td>7.7241(7)</td>
<td>1.962(8)</td>
<td>1.898(26)</td>
<td>159.5(26)</td>
<td>165.2(11)</td>
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<td>12.77</td>
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<tr>
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<td>5.4693(7)</td>
<td>5.4695(8)</td>
<td>7.7084(8)</td>
<td>1.974(8)</td>
<td>1.916(26)</td>
<td>154.9(20)</td>
<td>163.6(11)</td>
<td>17.95</td>
<td>13.31</td>
</tr>
<tr>
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<td>5.4690(4)</td>
<td>7.7140(6)</td>
<td>1.958(5)</td>
<td>1.971(21)</td>
<td>160.0(17)</td>
<td>161.9(9)</td>
<td>13.96</td>
<td>9.96</td>
</tr>
<tr>
<td>0.2</td>
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<td>5.4667(4)</td>
<td>7.7034(5)</td>
<td>1.961(4)</td>
<td>1.963(15)</td>
<td>158.3(12)</td>
<td>158.3(6)</td>
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<td>5.4777(2)</td>
<td>7.7017(3)</td>
<td>1.966(5)</td>
<td>1.984(14)</td>
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<td>5.4763(2)</td>
<td>7.6844(3)</td>
<td>1.965(5)</td>
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<td>155.8(13)</td>
<td>157.6(6)</td>
<td>15.38</td>
<td>10.89</td>
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and 132 K for x = 0, 0.1, 0.2, 0.25, and 0.3, respectively. The structure was identified to be single-phased orthorhombic with Pbnn space group by the X-ray diffraction patterns. The detailed structural parameters, as listed in Table 1, were obtained by the refinement of the X-ray diffraction data. In Table 1, the first column represents the Ca-concentration, the next three columns list the lattice parameters $a$, $b$, and $c$, respectively. The fifth column to the eight column give the local structural data of Mn-O-Mn octahedral. The last two columns are conventional weighted pattern ($R_{wp}$) and pattern ($R_p$) factors, respectively, denoting the agreement factors between the calculation pattern and the true data. According to these structural data, we plot out the structural parameters versus Ca-concentration in Figures 1 to 3. In Fig. 1, the lattice parameters $a$, $b$, and $c$ versus Ca-concentration is displayed with different symbols, where $c^* = c/\sqrt{2}$. It shows that $a$- as well as $c$-parameter decreases around 0.04 Å with increasing $y$ from 0 to 0.3; while $b$-parameter remains roughly a constant around 5.47 Å for $0 < y < 0.2$ and becomes $\sim$ 5.48 Å for $y \geq 0.2$. Since the $b$-parameter is more or less constant, the ratio of $a/b$ becomes smaller when $a$ decreases, suggesting a higher strain in the $a$-$b$ plane for higher $y$. For the change in the bond lengths of Mn-O, we have observed from Fig. 2 that the apical Mn-O bond length approximately does not change with $y$, but two planar M-O bond lengths change in the opposite directions with increasing $y$. Based on Fig. 2, an increase in one of the planar Mn-O bond length compensates the decrease of other planar Mn-O bond in the opposite direction. Together with Fig. 1, they imply that the replacement of a Sr-ion with a smaller Ca-ion induces the distortion in the $a$-$b$ plane of the unit cell and also the plane in Mn-O-Mn octahedral structure. Corresponding to the change in the bond-lengths, there is no systematic change
Fig. 1. Lattice parameters $a$, $b$ and $c^*$ versus Ca-concentration ($y$) for $\text{Pr}_{0.7}\text{Sr}_{0.3-y}\text{Ca}_y\text{MnO}_3$.

Fig. 2. Apical and planar Mn-O bond lengths versus Ca-concentration ($y$) for $\text{Pr}_{0.7}\text{Sr}_{0.3-y}\text{Ca}_y\text{MnO}_3$.

in the apical Mn-O-Mn bond angle (as seen in Fig. 3), but the planar Mn-O-Mn angle decreases systematically with increasing $y$. As a general argument, a larger mismatch between ions located at the $R$-site and the Mn-ion, usually causes Mn-O-Mn bond to bend and, as a result, this mismatch weakens the double exchange
interaction between Mn$^{+3}$ and Mn$^{+4}$, thus leading to a reduced $T_c$ and an increase in resistivity $\rho$. However, there is no discussion, in the conventional DE mechanism, for the field dependence of $T_c$ and $\rho$.

In Figs. 4 to 6, typical $\rho$ versus $T$ at various field were plotted at $y = 0, 0.1$ and 0.2, respectively. Different $\rho$–$T$ curves represent different fields from zero (top curve) to 1.6 tesla (bottom curve) with an interval of 0.4 tesla. For all samples we have measured except $y = 0.3$, the insulating to metallic phase transitions were observed. And, according to the magnetization data, they are all ferromagnetic at low temperature. Compared with the work done by Tomioka et al., there were
Fig. 5. Resistivity ($\rho$) versus Temperature ($T$) for Pr$_{0.7}$Sr$_{0.2}$Ca$_{0.1}$MnO$_3$.

Fig. 6. Resistivity ($\rho$) versus Temperature ($T$) for Pr$_{0.7}$Sr$_{0.1}$Ca$_{0.2}$MnO$_3$.

M–I transition for $y = 0, 0.175$ and $0.245$, and the charge-ordering occur for the sample with $y = 0.245, 0.28$ and $0.35$ in Pr$_{0.65}$Sr$_{0.35-y}$Ca$_y$MnO$_3$. In our Pr$_{0.7}$Sr$_{0.3-y}$Ca$_y$MnO$_3$ system, the Pr-concentration was fixed to be 0.7 instead of 0.65, and did not see any existence of charge-ordering over the examined range, $y = 0$ to $0.3$. Along with the fact that substituting Pr$^{+3}$ with Ca$^{+2}$ (or Sr$^{+2}$) is mainly to change the Mn-valence while replacing Sr$^{+2}$ by Ca$^{+2}$ is to change the effective radius of A-ion, our results suggest that the charge ordering is more sensitive to the Mn-valence than the radius of A-ion.

The M–I transition temperature ($T_m$) were found to be 245.7, 206.0, 166.8 and 106.1 K for $y = 0, 0.1, 0.2$ and $0.25$, respectively. Compared with the $T_c$ determined from the M–T curves, $T_m$ is lower than $T_c$ for $y = 0$ and $0.1$, but higher for $x = 0.2$ and $0.25$. It indicates that the resistive transition from insulating to metallic phase does not necessarily coincide with the magnetic transition from the paramagnetic
to ferromagnetic phase. This phenomenon is not peculiar if one examines all the existing $T_m$ and $T_c$ data for $(R, A)\text{MnO}_3$. However, it is hard to be explained based on the DE mechanism, in which the electrical conductivity is strong coupled with magnetic transition. As shown in the phase diagram of $\text{Pr}_{1-x}\text{Ca}_x\text{MnO}_3$, the samples with $x = 0.3$ sit on the boundary between the Ferromagnetic insulating and Antimagnetic insulating phases. In our data of $\text{Pr}_{0.7}\text{Ca}_{0.3}\text{MnO}_3$, we did observe the ferromagnetic insulating behavior. However, when we replaced Ca by Sr (partially or entirely) and kept the Pr-concentration, all samples became ferromagnetic metallic at low temperature. This phenomenon suggests that the size of A-ion have great effect on the electrical conductivity but less degree on the magnetic-ordering in $(R, A)\text{MnO}_3$.

It should be noted that the M-I transition is broader for low Ca-concentration and becomes narrower for high Ca-concentration. Since the X-ray results have shown the pure phases for all samples and that the Mn-O bond angle decreases with increasing Ca-concentration, the broadening may be cause by a stress-distribution associated with the size-mismatch between Pr-ion and (Ca, Sr)-ion. When Ca-concentration gets higher, the effective radius of (Ca, Sr) becomes smaller and closer to the radius of Pr-ion, thus the uniformity of the local stress in the lattices enhances.

As shown in Fig. 4 to 6, $T_m$ as well as $\rho$-value suppressed by increasing field. By defining the maximum MR value as $\Delta \rho/\rho_0$ and $\Delta \rho/\rho_0 = [\rho(T_m, 1.6 \text{ tesla}) - \rho(T_m, 0)]/\rho(T_m, 0)$, $\Delta \rho/\rho_0$ are 15, 25, and 48% for $x = 0, 0.1$ and 0.2, respectively.

In a recent paper by J. Fontcuberta et al., the value of MR at $T_m$ was found to be related to the mean value of R-radius, and was interpreted based on a model developed from that of Furukawa and Inoue et al. In this paper, the $t_{2g}$ and $e_g$ electrons of Mn-ions are treated as localized spins of $S = 3/2$, and itinerant electron of $S = 1/2$, respectively. The localized spins couple antiferromagnetically with each other and the strong Hund coupling acts between the localized spins and the itinerant electrons. And, there exist strong electron correlation among the itinerant electrons. A competition appears between a gain in the kinetic energy and a loss in the exchange energy of $t_{2g}$ spins which favor antiferromagnetic coupling. When the gain in the Kinetic energy overcomes the loss of the exchange energy, the transition from antiferromanetism to metallic ferromagnetism occurs. By means of the different approaches to calculate the conductivity, Furukawa and Inoue et al. reached the same equation describing the relation between MR and magnetization:

$$\frac{\rho(T, H)}{\rho(T, 0)} = 1 - B \left[ \frac{M(T, H)}{M_s} \right]^2,$$

where $M_s$ is the saturation magnetization, and $B = J/W$ with $J$ denoting the Hund coupling and $W$ the bandwidth. Equation (1) have been identified experimentally. According, in the case of fixing the carrier concentration (by fixing the ratio of Mn$^{+4}$/Mn$^{+3}$), the effect of the A-size on the crystal structure is mainly changing the Mn-O-Mn bond angle, resulting in a decrease in $W$, and, thus, an increase in
When B becomes larger, \(\rho(T, H)/\rho(T, 0)\) becomes smaller. Consequently, MR, defining as \(1 - \rho(T, H)/\rho(T, 0)\) becomes larger. This model is consistent with our observation that CMR effect enhances when the planar Mn-O-Mn bond angle reduces for high Ca-concentration.

4. Conclusion

In conclusion, we have measured the structural, resistivite, and magnetic properties on a series of \(\text{Pr}_{0.7}\text{Sr}_{0.3-y}\text{Ca}_y\text{MnO}_3\) samples. We have related the change in the lattice parameters, planar Mn-O bond length, and the planar Mn-O-Mn angles to the CMR values. Our results show, for the first time, that the planar Mn-O-Mn bond angle decreases systematically with increasing the concentration of Ca, resulting in a decrease in \(T_c\) and \(T_m\), and, an increase in CMR values. Based on the model of spin-disorder scattering, we thus attribute the enhancement of CMR in this system to the narrowing of the electronic bandwidth.

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References