

Temperature-dependent Magnetoresistance in Pr-based Manganites

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Systematic studies on $\text{Pr}_{0.7}\text{Sr}_{0.3-x}\text{Ca}_x\text{MnO}_3$, $\text{Pr}_{0.6}\text{Sr}_{0.4-y}\text{Ca}_y\text{MnO}_3$, $\text{Pr}_{0.5}\text{Sr}_{0.5-z}\text{Ca}_z\text{MnO}_3$, and Cr-doped $\text{Pr}_{0.6}\text{Sr}_{0.4}(\text{Mn}, \text{Cr})\text{O}_3$ reveal distinct origins of the magnetoresistance in Pr-based manganites. For $\text{Pr}_{0.7}\text{Sr}_{0.3-x}\text{Ca}_x\text{MnO}_3$ and $\text{Pr}_{0.6}\text{Sr}_{0.4-y}\text{Ca}_y\text{MnO}_3$, the sharp enhancement of the magnetoresistance ratio (MR) around the ferromagnetic transition temperature (T_c) indicates a percolative field-induced transition. For $\text{Pr}_{0.5}\text{Sr}_{0.5-z}\text{Ca}_z\text{MnO}_3$, the MR peak appears at the charge ordering temperature instead of T_c , and the low-field MR shows a different behavior from those of $\text{Pr}_{0.7}\text{Sr}_{0.3-x}\text{Ca}_x\text{MnO}_3$ and $\text{Pr}_{0.6}\text{Sr}_{0.4-y}\text{Ca}_y\text{MnO}_3$, suggesting that the relative population of ferromagnetic and antiferromagnetic domains governs the temperature dependent MR behavior. For Cr-doped $\text{Pr}_{0.6}\text{Sr}_{0.4}(\text{Mn}, \text{Cr})\text{O}_3$, the metal-insulator transition is shifted to a lower temperature with an enhancement of MR. Remarkably, it retains a weakly temperature-dependent character, which may be correlated with the spin scattering mechanism due to the presence of Cr-impurities.

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I. Introduction

The (Re, A) MnO_3 (Re = rare earth elements, A = Ca, Sr, Ba) perovskites exhibit complicated magnetic and structure phases depending on the doping concentration [1]. The coincidence of the ferromagnetic transition temperature (T_c) and the insulator-metal transition temperature (T_m) was explained by the double exchange model, which was improved later by incorporating the Jahn-Teller effect [2]. On the other hand, the discovery of the colossal magnetoresistance (CMR) in these compounds has raised interest regarding its potential application for magnetic sensors or devices. However, several obstacles have been encountered during the past decade. First, the high magnetoresistance ratio (MR) is only available at low temperatures, and attempts to increase T_c always lead to a reduction of MR [3]. Second, the high coercive field (> 1 T) of CMR oxides makes them less promising for low-field sensors [4]. Third, their strong temperature dependence character results in an unstable electronic signal for magnetic devices [5].

Many efforts have been made to overcome these obstacles. It was reported that polycrystalline samples with larger grain size exhibited a higher MR than those of single crystals [6]. Magnetic field dependent studies revealed that the grain boundary effect was especially sensitive to low fields [6, 7]. However, the underlying mechanism for the grain boundary effect, i.e. whether it is spin tunneling [6] or spin scattering [8], remains unclear. On the other hand, based on the percolative character exhibited in CMR oxides [9], an enhancement of room temperature MR was

achieved [10]. Composites such as $\text{La}_{0.7}\text{Sr}_{0.3}\text{MnO}_3/\text{glass}$ [11] and $\text{La}_{2/3}\text{Sr}_{1/3}\text{MnO}_3/\text{CeO}_2$ [12] have been made to demonstrate a field-induced percolative transition. Other methods, such as the tunneling junction were also invented to demonstrate the spin tunneling effect [13]. For these devices, high quality CMR films are demanded for further improvement. To date, although various CMR mechanisms have been proposed, a complete model is still lacking for the description of a universal relation between the underlying effects and the corresponding compounds.

Here we report on a systematic study of four series of Pr-based manganites. Our results indicate that the MR behavior for different systems can be classified into three kinds. First, for $\text{Pr}_{0.7}\text{Sr}_{0.3-x}\text{Ca}_x\text{MnO}_3$ and $\text{Pr}_{0.6}\text{Sr}_{0.4-y}\text{Ca}_y\text{MnO}_3$, the MR vs. temperature (T) relation is dominated by their percolative nature. Second, although MR(T) of $\text{Pr}_{0.5}\text{Sr}_{0.5-z}\text{Ca}_z\text{MnO}_3$ shows percolative features, its origin is attributed to the competition between ferromagnetic and anti-ferromagnetic domains. Regarding the ionic size-effect (average ionic size of $(\text{Pr}_{1-x}(\text{Sr}, \text{Ca})_x)$) on charge ordering, the MR(T) of $\text{Pr}_{0.5}\text{Sr}_{0.5-z}\text{Ca}_z\text{MnO}_3$ shows a different behavior from those of the $\text{Pr}_{0.7}\text{Sr}_{0.3-x}\text{Ca}_x\text{MnO}_3$ and $\text{Pr}_{0.6}\text{Sr}_{0.4-y}\text{Ca}_y\text{MnO}_3$ systems. For Cr-doped compounds, the insulator-metal transition is induced at a lower temperature, but the MR does not show a corresponding peak at T_m . Therefore, not only is MR enhanced in Cr-doped compounds, but the weak temperature dependency is also retained. Overall, we have identified three different kinds of underlying CMR mechanisms for various Pr-based manganites.

II. Experiments

Samples of $\text{Pr}_{0.7}\text{Sr}_{0.3-x}\text{Ca}_x\text{MnO}_3$, $\text{Pr}_{0.6}\text{Sr}_{0.4-y}\text{Ca}_y\text{MnO}_3$, $\text{Pr}_{0.5}\text{Sr}_{0.5-z}\text{Ca}_z\text{MnO}_3$ and Cr-doped $\text{Pr}_{0.6}\text{Sr}_{0.4}(\text{Mn}, \text{Cr})\text{O}_3$ were synthesized by the solid state reaction of high purity powders of Pr_6O_{11} , SrCO_3 , CaCO_3 , Cr_2O_3 and MnCO_3 . Pr_6O_{11} powder was first dried at 950°C for 3 hours and then mixed with other powders in appropriate ratios. The mixed powders were well-ground, pelletized, and heated at 1100°C to 1400°C for 16 hours. The high temperature treatment was repeated three times. All compositions were identified as single phases by their X-ray diffraction (XRD) patterns. The structures of $\text{Pr}_{0.7}\text{Sr}_{0.3-x}\text{Ca}_x\text{MnO}_3$ and $\text{Pr}_{0.6}\text{Sr}_{0.4-y}\text{Ca}_y\text{MnO}_3$ were investigated by Rietveld refinement based on the XRD profiles and the detailed structure data have been published elsewhere [14]. Resistance R is measured using the standard four-point method and MR is defined as $[R(0) - R(5\text{ T})] / R(0) \times 100\%$.

III. Results and discussion

Figure 1 displays the resistivity vs. temperature T for $\text{Pr}_{0.7}\text{Sr}_{0.3-x}\text{Ca}_x\text{MnO}_3$ with $x = 0$ to 0.3. This indicates that the insulating to metallic (M-I) transition temperature decreases with increasing x , and there is no M-I transition for $x = 0.3$. Fig. 2 and 3 show the MR vs. T for $\text{Pr}_{0.7}\text{Sr}_{0.3-x}\text{Ca}_x\text{MnO}_3$ and $\text{Pr}_{0.6}\text{Sr}_{0.4-y}\text{Ca}_y\text{MnO}_3$, respectively. Arrows in both figures indicate the corresponding curie temperature T_c for each curve. It is obvious that the peak position of each MR(T) curve coincides with T_c in $\text{Pr}_{0.7}\text{Sr}_{0.3-x}\text{Ca}_x\text{MnO}_3$. For $\text{Pr}_{0.6}\text{Sr}_{0.4-y}\text{Ca}_y\text{MnO}_3$ it appears at a lower temperature than their corresponding T_c , however, the deviation is less than 10 K for all curves. It is noteworthy, MR(T) for $y = 0$ has a weak temperature dependence. For both $\text{Pr}_{0.7}\text{Sr}_{0.3-x}\text{Ca}_x\text{MnO}_3$ and $\text{Pr}_{0.6}\text{Sr}_{0.4-y}\text{Ca}_y\text{MnO}_3$ systems, the peak value of the MR increases and T_c decreases with increasing Ca concentration. Recent studies have indicated that, for CMR oxides with low T_c 's, the transport behavior is percolative in character and can be expressed by

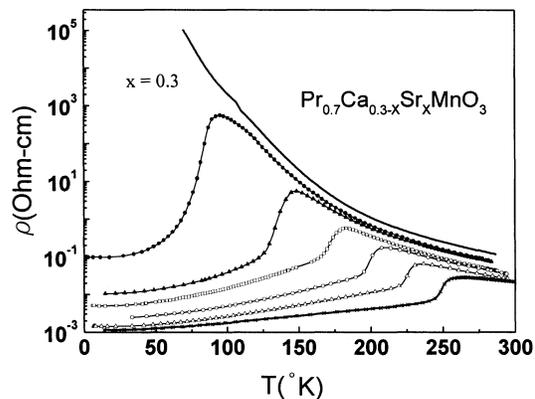


FIG. 1. Resistivity ρ vs. temperature T for $\text{Pr}_{0.7}\text{Sr}_{0.3-x}\text{Ca}_x\text{MnO}_3$, with $x = 0$ to 0.3 with respect to the curve from bottom to the top.

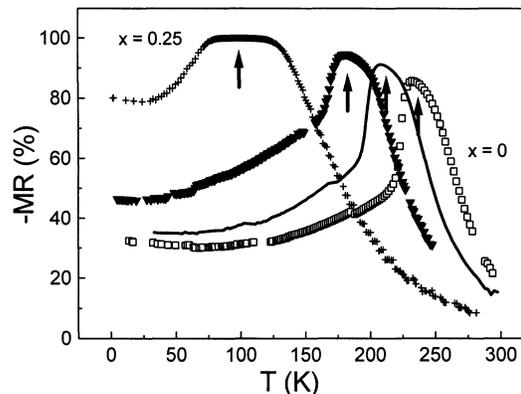


FIG. 2. MR vs. T for $\text{Pr}_{0.7}\text{Sr}_{0.3-x}\text{Ca}_x\text{MnO}_3$, with $x = 0, 0.1, 0.2$ and 0.25 . The arrows denote the corresponding T_c for each curve.

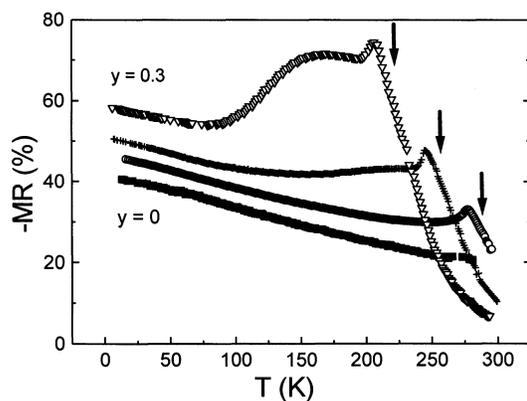


FIG. 3. MR vs. T for $\text{Pr}_{0.6}\text{Sr}_{0.4-y}\text{Ca}_y\text{MnO}_3$ with $y = 0, 0.1, 0.2$ and 0.3 . The arrows denote the corresponding T_c for each curve.

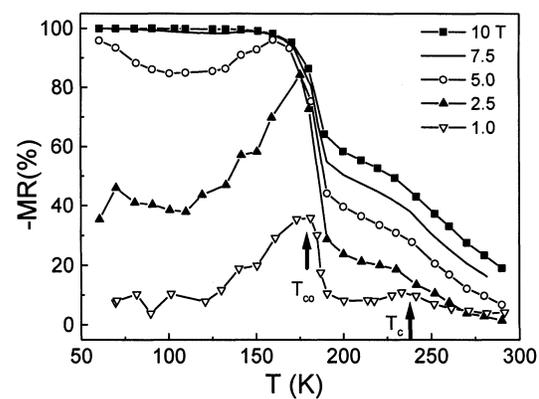


FIG. 4. Evolution of MR vs. T with respect to different fields for $\text{Pr}_{0.5}\text{Sr}_{0.5-z}\text{Ca}_z\text{MnO}_3$ with $z = 0.2$.

the formulation of the effective medium theories for binary insulator-metal mixtures [9]. The percolative transition is considered to be sensitive to the relative population of insulating and metallic domains, and the population has been correlated with their magnetization [9]. Therefore, a field-induced percolative transition is only observed in the temperature region where the relative population of insulating and metallic domains is near the percolation threshold. As shown in Figs. 1 and 2, for both $\text{Pr}_{0.7}\text{Sr}_{0.3-x}\text{Ca}_x\text{MnO}_3$ and $\text{Pr}_{0.6}\text{Sr}_{0.4-y}\text{Ca}_y\text{MnO}_3$, the MR is enhanced greatly in a narrow temperature region around T_c , which is qualitatively consistent with a percolative character.

Figure 4 shows the typical evolution of MR(T) with different magnetic fields for $\text{Pr}_{0.5}\text{Sr}_{0.3-z}\text{Ca}_z\text{MnO}_3$ with $z = 0.2$. For $H > 7.5$ T, the charge ordering state is collapsed and a nearly 100% MR is obtained at low temperature. Interestingly, for $H < 5$ T, the MR has high values in a narrow temperature range around T_{co} (175 K) instead of around T_c (235 K), which suggests that

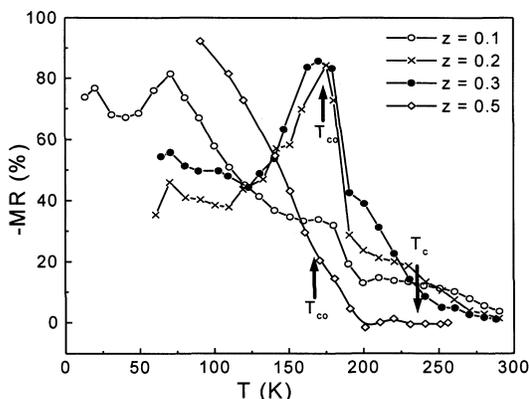


FIG. 5. MR vs. temperature relation for $z = 0.1$, 0.2 , 0.3 , and 0.5 under $H = 2.5$ T. The arrows denote T_c and T_{co} .

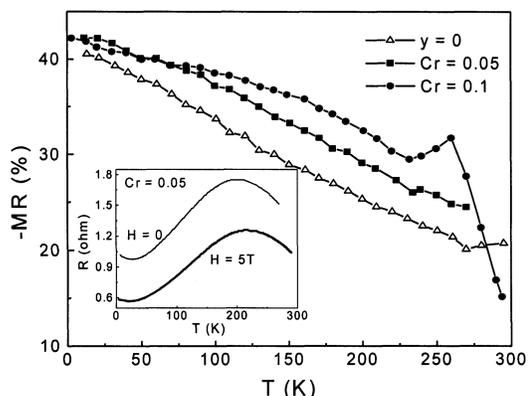


FIG. 6. MR vs. T of $\text{Pr}_{0.6}\text{Sr}_{0.4}\text{Mn}_{0.95}\text{Cr}_{0.05}\text{O}_3$, $\text{Pr}_{0.6}\text{Sr}_{0.4}\text{Mn}_{0.9}\text{Cr}_{0.1}\text{O}_3$, and $\text{Pr}_{0.6}\text{Sr}_{0.4}\text{MnO}_3$ for comparison. The inset shows the magnetic field effect ($H = 5$ T) for $\text{Pr}_{0.6}\text{Sr}_{0.4}\text{Mn}_{0.95}\text{Cr}_{0.05}\text{O}_3$.

the field-induced percolative transition is more sensitive at the charge ordering (antiferromagnetic) transition rather than at the ferromagnetic transition. For $H = 1$ T, a slight enhancement of MR is observable at 235 K, demonstrating that the percolative nature is still effective at T_c . However, the fact that the peak value of $\text{MR}(T)$ under 1 T is much larger at T_{co} than at T_c suggests that the field-induced percolative transition is more effective near the boundary of ferromagnetic and antiferromagnetic domains.

As we have mentioned, the sensitivity of the field-induced percolative transition is determined by the relative population of insulating and metallic domains. For $\text{Pr}_{0.5}\text{Sr}_{0.5-z}\text{Ca}_z\text{MnO}_3$, our earlier work has shown that the relative population depends crucially on the Ca concentration [15]. The result that the thermal hysteresis is larger for $z = 0.3$ and 0.4 than that for $z = 0.1$ and 0.5 indicates that the relative ferromagnetic-antiferromagnetic population is not a monotonic function of z . The critical behavior also manifests itself in Fig. 5. In contrast to the $\text{MR}(T)$ shown in Fig. 1, a stronger competition between ferromagnetic and antiferromagnetic domains for $z = 0.2$ and 0.3 results in a larger MR value than that for $z = 0.1$ and 0.5 at their corresponding T_{co} ($T_{co} = 170, 180$, and 240 K for $z = 0.1, 0.3$ and 0.5 , respectively).

More interesting MR behaviors are observed in Cr-doped $\text{Pr}_{0.6}\text{Sr}_{0.4}(\text{Mn}, \text{Cr})\text{O}_3$ as shown in Fig. 6. Although Cr^{3+} has the same electronic configuration as Mn^{4+} , it has been reported that doping Cr into $\text{La}_{0.7}\text{Ca}_{0.3}\text{MnO}_3$ interrupts the double exchange interaction [16]. Namely, the Cr dopant acts as an impurity and destroys the interaction between the Mn^{3+} - Mn^{4+} networks. The inset of Fig. 6 shows the typical field-dependent $\rho(T)$ for Cr-doped $\text{Pr}_{0.6}\text{Sr}_{0.4}(\text{Mn}, \text{Cr})\text{O}_3$. As expected, R increases and the insulating to metallic transition temperature T_m decreases to 201 K by Cr-doping in $\text{Pr}_{0.6}\text{Sr}_{0.4}\text{Mn}_{0.95}\text{Cr}_{0.05}\text{O}_3$ ($T_m = 250$ K for $\text{Pr}_{0.6}\text{Sr}_{0.4}\text{MnO}_3$). The magnetic field of 5 T reduces the resistance to a lower value and shifts T_m to 217 K. Surprisingly, as shown in Fig. 6, when converting to the MR value, it does not show a peak corresponding peak to those observed in Figs. 2 and 3. Similar effects also apply for $\text{Pr}_{0.6}\text{Sr}_{0.4}\text{Mn}_{0.9}\text{Cr}_{0.1}\text{O}_3$, its T_m reduces to 170 K for a higher Cr concentration; however, the MR shows no peak around 170 K. Remarkably,

the weakly temperature dependent MR behavior in $\text{Pr}_{0.6}\text{Sr}_{0.4}\text{MnO}_3$ (shown in Fig. 6 and also in Fig. 3 for $y = 0$) is also exhibited by the Cr-doped compounds. These unusual behaviors indicate that the percolative nature does not dominate in the Cr-doped compounds; instead, spin scattering due to Cr dopants must play an important role. Recently, the impurity-substituted manganite $\text{Nd}_{0.5}\text{Ca}_{0.5}(\text{Mn}, \text{Cr})\text{O}_3$ has been proposed to behave as a *relaxor ferromagnet* [17], i.e. the Cr impurity serves as an independent ferromagnetic microembryo and grows with increasing external field. From this point of view, an extra temperature-independent term due to Cr-scattering should be added to the original MR vs. T relation. Although the metallic character, via the double exchange between Mn^{3+} - Mn^{4+} networks, is destroyed by the Cr dopant, the metallic state can be gradually recovered with decreasing temperature, and the insulator-metal transition is driven by a diffusive connection of such ferromagnetic-metallic microembryos. Further work is required to characterize the unusual behavior of Cr-doped $\text{Pr}_{0.6}\text{Sr}_{0.4}(\text{Mn}, \text{Cr})\text{O}_3$.

IV. Conclusion

Our studies on the temperature dependency of MR in Pr-based manganites reveal three different features for different compounds. First, for $\text{Pr}_{0.7}\text{Sr}_{0.3-x}\text{Ca}_x\text{MnO}_3$ and $\text{Pr}_{0.6}\text{Sr}_{0.4-y}\text{Ca}_y\text{MnO}_3$, the field-induced percolative effect can yield a large MR around T_c . Second, for a system with a charge ordering transition (such as $\text{Pr}_{0.5}\text{Sr}_{0.5-z}\text{Ca}_z\text{MnO}_3$) the MR is more sensitive at T_{co} than at T_c and is crucially dependent on the relative population of the ferromagnetic and the antiferromagnetic domains. Third, for the Cr-doped $\text{Pr}_{0.6}\text{Sr}_{0.4}(\text{Mn}, \text{Cr})\text{O}_3$, the MR can be increased by adding Cr impurities, and the feature of weak temperature-dependence in $\text{Pr}_{0.6}\text{Sr}_{0.4}\text{MnO}_3$ is preserved in the Cr-doped compounds.

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