

# Lattice effect on ferromagnetic-metal phase transition in $\text{Pr}_{0.65}\text{Ca}_{0.35}(\text{Mn}_{1-Z}\text{Co}_Z)\text{O}_3$ and $\text{Pr}_{0.65}\text{Ca}_{0.35}(\text{Mn}_{1-Z}\text{Cr}_Z)\text{O}_3$

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## Abstract

The lattice effects have been studied on the transition to ferromagnetic-metal state caused by Co, Cr and Ni doping in  $\text{Pr}_{0.65}\text{Ca}_{0.35}\text{MnO}_3$ . The contrasting behavior of the thermal expansion  $L(T)/L_{20}$  and the phonon thermal conductivity  $\kappa_{\text{ph}}(T)$  observed for Co and Cr (Ni) doping is attributable to the difference in the charge order (CO) states, i.e., long-ranged (Co-doping) CO or short-ranged (Cr-, Ni-doping) one. The nonmagnetic low spin state of doped  $\text{Co}^{3+}$  ions in the insulating CO phase may be a possible origin to make the difference.

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## 1. Introduction

In the perovskite-type manganites  $\text{RE}_{1-X}\text{AE}_X\text{MnO}_3$  (RE = La, Pr, Nd etc., AE = Ba, Sr, Ca), the competition of the ferromagnetic-metal (FM-M) phase and the charge-ordered (CO) insulator phase stages intriguing physical properties such as the colossal magnetoresistance (CMR). Because of the narrow electron bandwidth  $W$  due to the small ionic radii of Pr and Ca, the CO phase is stabilized in  $\text{Pr}_{1-X}\text{Ca}_X\text{MnO}_3$  over a wide range of the carrier concentration  $X$  ( $0.30 < X \leq 0.75$ ) [1,2] and the ferromagnetic insulating (FM-I) phase appears for  $X \leq 0.30$ . The CO state, however, is not quite stable and the FM-M phase is realized for  $0.30X \leq 0.50$  by applying the magnetic field  $H$  or by doping a small amount (2–4%) of other 3d-transition metal element (M) at Mn sites. In this note, we study the induced transition to the FM-M phase in  $\text{Pr}_{0.65}\text{Ca}_{0.35}(\text{Mn}_{1-Z}\text{M}_Z)\text{O}_3$  (M = Co, Cr, Ni). Because the Jahn–Teller (J–T) lattice distortions around  $\text{Mn}^{3+}$  spins are considered to be an important key factor to

determine the physical properties of the present system, we investigate the lattice effect by measuring the thermal expansion and the phonon thermal conduction.

## 2. Results and discussion

$\text{Pr}_{0.65}\text{Ca}_{0.35}(\text{Mn}_{1-Z}\text{M}_Z)\text{O}_3$  polycrystals were prepared from stoichiometric mixtures of  $\text{Pr}_6\text{O}_{11}$ ,  $\text{CaCO}_3$ ,  $\text{Mn}_3\text{O}_4$  and CoO (CrO, NiO) powders by a standard solid-state reaction method [3]. The electrical resistivity  $\rho(T)$  was measured by a four-terminal method and the magnetization  $M(T)$  was measured by a SQUID magnetometer. The thermal expansion  $L(T)/L_{20}$  (= the sample length at temperature  $T$  normalized by that at 20 K) was measured by a strain gauge method. The thermal conductivity  $\kappa(T)$  was measured by a continuous heat flow method.

Fig. 1(a) shows  $M(T)$  of  $\text{Pr}_{0.65}\text{Ca}_{0.35}(\text{Mn}_{0.96}\text{M}_{0.04})\text{O}_3$  (PCMO(M)) under the field of 0.5 T. The  $M(T)$  curves for PCMO(Cr) and PCMO(Ni) gradually increases below  $T_c$  like a usual ferromagnet with second-order FM transition. In contrast,  $M(T)$  of PCMO(Co) almost jumps up at  $T_c$  with decreasing  $T$ , which is indicative of a typical first-order transition. Fig. 1(b) presents  $\rho(T)$  of respective samples. All the samples

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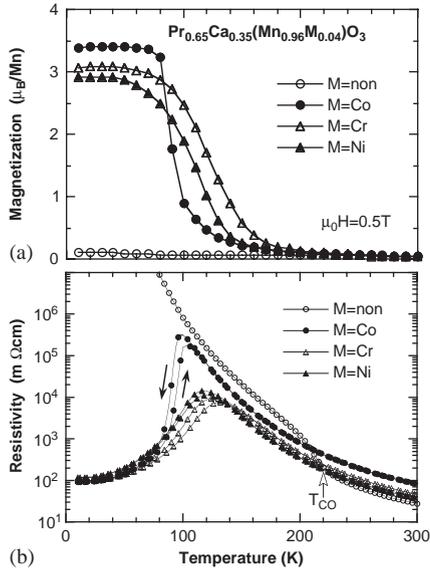


Fig. 1. (a)  $M(T)$  and (b)  $\rho(T)$  for the  $\text{Pr}_{0.65}\text{Ca}_{0.35}(\text{Mn}_{1-z}\text{M}_z)\text{O}_3$  samples ( $M = \text{non}, \text{Co}, \text{Cr}, \text{Ni}$ ).

exhibit metal–insulator (M–I) transition, taking a  $\rho(T)$  maximum in the vicinity of  $T_c$ . The  $\rho(T)$  curves of PCMO(Cr) and PCMO(Ni) are very much alike and the M–I transitions are rather gradual. It is to be noticed, however, that  $\rho(T)$  exhibits a clear hysteresis between cooling and heating scans. In contrast, PCMO(Co) shows a very sharp M–I transition, which is also accompanied by a hysteresis.

Fig. 2(a) shows  $L(T)/L_{20}$  of PCMO(Co) and PCMO(Cr), where we notice much contrasting behaviours. With decreasing  $T$ ,  $L(T)/L_{20}$  of PCMO(Co) exhibits a sharp shrink at  $T_c$ , while the corresponding shrink is absent for PCMO(Cr). The shrink is also absent for PCMO(Ni). The sharp shrink of  $L(T)/L_{20}$  was observed for  $\text{La}_{1-x}\text{Ca}_x\text{MnO}_3$  at the first order-like M–I transition and was attributed to the release of the J–T lattice distortions in the metallic phase [4]. Fig. 2(b) displays  $\kappa(T)$  vs.  $T$ . The heat conduction in the present specimens is overwhelmingly due to phonons because of the large  $\rho(T)$ . With decreasing  $T$ ,  $\kappa(T)$  of PCMO(Co) is enhanced step-like at  $T_c$ , while very gradual  $\kappa$  enhancement is barely noticeable for PCMO(Cr). The  $\kappa$  enhancement in the FM–M phase has been explained as to originate from the reduction of phonon scattering by local J–T distortions [5].

Now, we briefly discuss the origin of the difference in the FM–M transitions. In the present PCMO system, the FM–M phase is realized at an expense of the CO state damage caused by the 3d-element doping. By the electron microscope measurement, Katsufuji et al. [6] observed the change of the long-ranged CO to the short-ranged one as a result of Cr doping. The short-ranged CO is consistent with our observation for PCMO(Cr)

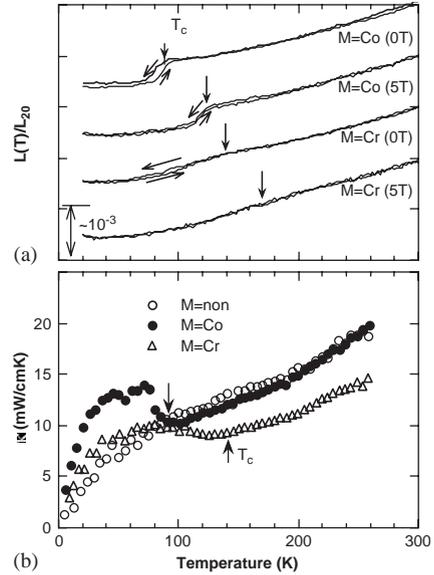


Fig. 2. (a)  $L(T)/L_{20}$  and (b)  $\kappa(T)$  for the  $\text{Pr}_{0.65}\text{Ca}_{0.35}(\text{Mn}_{1-z}\text{M}_z)\text{O}_3$  samples ( $M = \text{non}, \text{Co}, \text{Cr}$ ).

and PCMO(Ni) but the present results for PCMO(Co) suggest that the long-ranged CO may survive after Co-doping. It is widely accepted that the ground state of  $\text{Co}^{3+}$  ions in insulating  $\text{LaCoO}_3$  is nonmagnetic low-spin state. The  $\text{Co}^{3+}$  low-spin state should be more stable in the PCMO system because of the stronger crystalline field due to the smaller lattice parameter. The origin of the survival of long-ranged CO may be ascribed to nonmagnetic  $\text{Co}^{3+}$  because the local (magnetic) interaction with neighbouring Mn spins should be then by far weaker. In the FM–M phase of  $\text{La}_{1-x}\text{Sr}_x\text{CoO}_3$ , the intermediate Co spin state is known to be stabilized. It is very intriguing to elucidate the Co spin state in the FM–M phase of PCMO(Co). The larger saturation moment of PCMO(Co) than PCMO(Cr) and PCMO(Ni) in Fig. 1(a) may imply the magnetic Co ions in the FM–M phase. The microscopic study for PCMO(Co) is necessary.

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