



Magic d-electron number of doped ions for occurrence of ferromagnetic metal phase in $\text{Pr}_{0.65}\text{Ca}_{0.35}\text{Mn}_{0.96}\text{A}_{0.04}\text{O}_3$

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Abstract

The electrical resistivity ρ , Seebeck coefficient S and magnetization M have been measured for polycrystalline $\text{Pr}_{0.65}\text{Ca}_{0.35}\text{Mn}_{0.96}\text{A}_{0.04}\text{O}_3$ -doped with a vast variety of elements A. The ferromagnetic metal (FM) phase has been caused by doping only by Cr, Co, Ni, Ru and Ir. A necessary condition for the electronic configuration of the dopants has been clarified to materialize the FM phase in this system.

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1. Introduction

The perovskite-type manganites, $\text{RE}_{1-X}\text{AE}_X\text{MnO}_3$ (RE = La, Pr, etc., AE = Ba, Sr, Ca, etc.), exhibit intriguing physical properties, which originate from the competition between superexchange (SE), double exchange (DE) and charge order (CO)–orbital order (OO). In $\text{Pr}_{1-X}\text{Ca}_X\text{MnO}_3$ with rather small A-site ion radii of Pr^{3+} and Ca^{2+} , the

ferromagnetic-metal (FM) phase does not actualize owing to the narrow one electron bandwidth. The phase boundary between ferromagnetic-insulator (FI) and CO–OO phases is located at $X \sim 0.30$, the CO–OO phase being stable for $X \geq 0.35$. The hidden FM phase shows up for $X \geq 0.35$ under an applied magnetic field or with the Mn-site doping by suitable cations. In order to realize the FM phase, it is necessary for the dopants to efficiently destroy CO–OO without seriously damaging the DE mechanism. We have studied the 4%-doping effect of various cation dopants in $\text{Pr}_{0.65}\text{Ca}_{0.35}\text{MnO}_3$ (PCMO). This composition was

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selected because the free energies of the CO-, FM- and FI-phase are nearly degenerate.

$\text{Pr}_{0.65}\text{Ca}_{0.35}\text{Mn}_{0.96}\text{A}_{0.04}\text{O}_3$ (A-PCMO) polycrystals were prepared by a solid-state reaction method (A = Mg, Ti, V, Cr, Fe, Co, Ni, Cu, Zn, Ga, Zr, Nb, Mo, Ru, Rh, Pd, Ag, In, Sn, Ta, Ir). We performed detailed Rietveld analyses for the powder X-ray diffraction to determine the lattice parameter change due to the doping.

2. Results and discussion

Fig. 1(a) shows the electrical resistivity $\rho(T)$ of the Cr-, Co-, Ni-, Ru- and Ir-PCMO as a function of temperature T . The spontaneous CO–FM phase transition is exhibited for these dopants. Other dopants have proved to cause no insulator–metal (I–M) transition.

Fig. 1(b) presents the Seebeck coefficient S vs. T for the respective samples. $S(T)$ curves rapidly drop toward $S = 0$ level around the I–M transition temperature T_{IM} . The rapid reduction of $S(T)$ confirms the bulk nature of the I–M transition. For all the other cation doping, $S(T)$ diverges with decreasing T .

Fig. 1(c) shows the magnetization $M(T)$ under the field of 0.5 T. The $M(T)$ values of Cr-, Co-, Ni- and Ru-PCMO reach about $3\mu_{\text{B}}/\text{Mn}$ at low T , while $M(T)$ of Ir-PCMO remains somewhat smaller ($\sim 2.4\mu_{\text{B}}/\text{Mn}$).

Let us discuss the mechanism of the appearance of the FM phase in the present PCMO system. Hebert et al. [1] pointed out the importance of impurity e_{g} level at the impurity site: hopping electrons must take advantage of the extended empty e_{g} orbital of the dopant to preserve the DE mechanism. In this paper, we propose a necessary condition, for the FM phase occurrence: *the available e_{g} orbit must be energetically lowest*.

Based on the Rietveld analyses, we have determined the lattice parameter variation on the doping amount [2]. This process enabled us to fix the valence state of the majority of the cation dopants. The key result is that Co and Ni are in 3+ valency and are in low spin (LS) configuration (see Fig. 2). In Fig. 2, we can see that among the 3d transition element, the Co^{3+} (LS), Ni^{3+} (LS) and

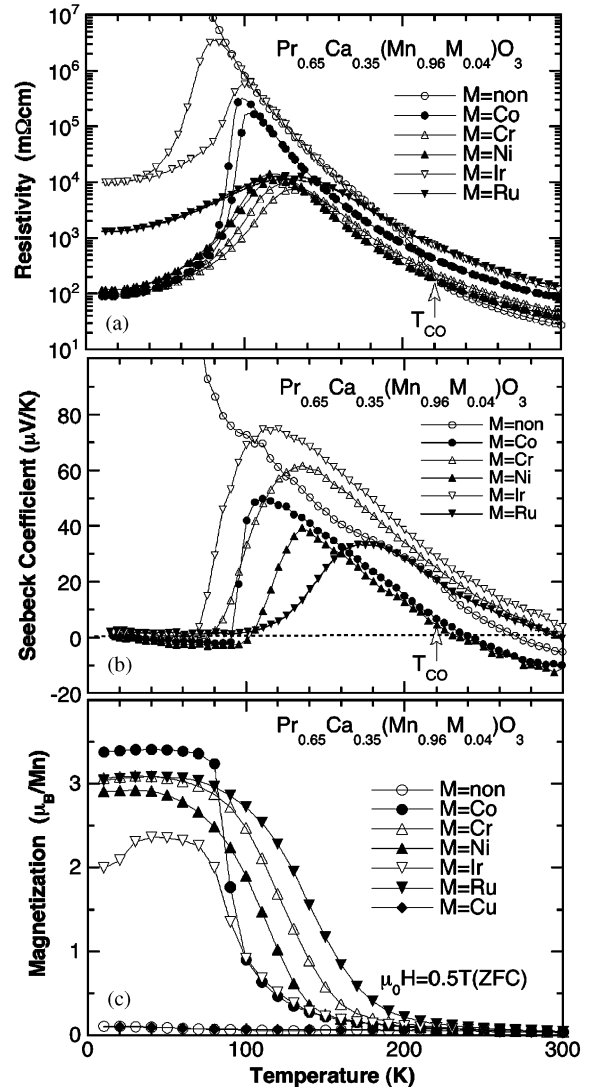


Fig. 1. (a) $\rho(T)$, (b) $S(T)$ and (c) $M(T)$ as functions of temperature T . T_{CO} denotes the CO transition temperature in $\text{Pr}_{0.65}\text{Ca}_{0.35}\text{MnO}_3$.

high-spin Cr^{3+} (HS) satisfy the necessary condition. The valencies of other 3d transition elements are Ti^{4+} , V^{3+} and Fe^{3+} (HS), which are not compatible with the condition. The 5d transition element Ir^{3+} is in isomorphous d electron configuration as Co^{3+} (LS) and exhibits the I–M transition.

As is well known, Ru is a strong dopant to stage the FM phase in manganites [3]. The Rietveld

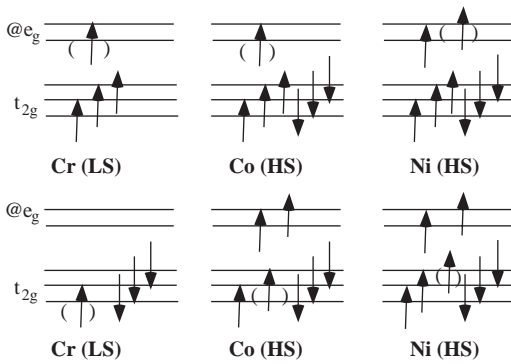


Fig. 2. Spin configuration of Cr^{3+} , Co^{3+} and Ni^{3+} . The spins in the parenthesis indicate the level to be occupied by the transient hopping electron. The upper row is compatible with the ferromagnetic metal phase formation.

analyses have supported the Ru^{4+} valency with $4d^4$ electron configuration, which is isomorphous with the parent Mn^{3+} configuration. It is generally believed that the 4d and 5d transition metal elements tend to take the LS configuration in crystals. Our necessary condition demands that Rh^{4+} should be in the HS configuration or, at least, the HS configuration should be almost

degenerate energetically with the LS configuration in Rh-PCMO.

The lattice parameter analyses suggest Cu^{3+} valency, which is compatible with the condition, but the I–M transition does not take place. In Fig. 1(c), $M(T)$ curve of Cu-PCMO is quite small and almost falls on the pristine PCMO. The CO–OO is hardly damaged by the Cu^{3+} dopants, which may be the origin of the absence of the FM phase in Cu-PCMO.

In summary, we determined the spin configurations of Co and Ni dopant as the low spin t_{2g} and $t_{2g}^6 e_g^1$, respectively, from the analyses on the lattice parameter change upon doping in $\text{Pr}_{0.65}\text{Ca}_{0.35}\text{MnO}_3$. The result leads us to a rigorous necessary condition for the occurrence of the spontaneous ferromagnetic-metal phase, i.e., the dopant must have empty e_g -orbital energetically lowest.

References

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- [2] To be reported elsewhere.
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