



# Universal effect of Mn-site doping on charge ordering in $\text{La}_{1/3}\text{Ca}_{2/3}\text{MnO}_3$



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## ABSTRACT

Comparison of doping effect on the charge ordering in  $\text{La}_{1/3}\text{Ca}_{2/3}\text{Mn}_{1-y}\text{M}_y\text{O}_3$  ( $M$ : Fe, Ga, Cr, Ni, Cu, Ru, Mg and  $0 \leq y \leq 0.07$ ) has been investigated by combining magnetic and transport measurements and local compositional analysis *in situ* in transmission electron microscope. The effect of Mn-site doping on the charge ordering temperature  $T_{CO}$  is shown for the first time to be universal for a given dopant valence and  $y \leq 0.05$ .  $T_{CO}$  is governed by the effective relative concentration  $n_{\text{Mn}^{3+}} = \text{Mn}^{3+}/(\text{Mn}^{3+} + \text{Mn}^{4+})$  of  $\text{Mn}^{3+}$  ions,  $T_{CO} \sim C n_{\text{Mn}^{3+}}$ , where the coefficient  $C$  depends on the valence but not on  $d$ -shell filling of a dopant ion. This dependence indicates that any of the considered dopants do not participate in charge transfer during charge ordering formation, however, indirectly affects the charge redistribution between manganese ions. Consideration of Mn-site doping effect on charge ordering temperature using a simple order–disorder model supports the concept of universality for a given dopant valence and dominating role of the factor of entropy over energy change. Analysis of the remanent magnetization together with the obtained behavior of  $T_{CO}(n_{\text{Mn}^{3+}})$  testify that it is the dopant valence ( $\text{Ru}^{5+}$ ), but not formation of Ru-based magnetic clusters, that is responsible for antiferromagnetic (AFM) insulator–ferromagnetic (FM) ‘bad-metal’ phase transition observed in the Ru-doped system at  $y = 0.07$ .

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## 1. Introduction

The colossal magnetoresistance (CMR) of the perovskite manganites  $\text{Ln}_{1-x}\text{A}_x\text{MnO}_3$  ( $\text{Ln} = \text{La, Nd, Pr, etc.}$  and  $A = \text{Ca, Sr, Ba, etc.}$ ) was observed first in the hole-doped manganites ( $x < 0.50$ ), where it coincides with a paramagnetic insulating to ferromagnetic metallic transition and is mainly based on the double exchange mechanism [1] between the  $\text{Mn}^{3+}$  and  $\text{Mn}^{4+}$  ions and Jahn–Teller effect of  $\text{Mn}^{3+}$  [2]. The effect of CMR can be also obtained in the half-doped manganites, for instance, in  $\text{Pr}_{0.5}\text{Sr}_{0.5}\text{MnO}_3$  [3], however, appearance of metallicity and FM requires the destruction of the low temperature AFM phase by applying a magnetic field. In this case the induced CMR is considered to result from the competition between FM metallic and AFM insulating domains [4–6].

Since  $\text{Mn}^{3+} - \text{O}^{2-} - \text{Mn}^{4+}$  chain is responsible for wide variety of physical behavior of the manganites, the Mn-site doping can strongly affect these properties, including initiation of the CMR. Namely, doping of the charge-ordered manganite  $\text{Pr}_{0.5}\text{Ca}_{0.5}\text{MnO}_3$  with Cr, Co, and Ni induces an insulator–metal transition even in the absence of a magnetic field [7–9]. Ru doping induces

metallicity and ferromagnetism in a number of the manganite systems, for example in  $\text{Pr}_{0.5}\text{Ca}_{0.5}\text{MnO}_3$  and  $\text{Pr}_{0.5}\text{Sr}_{0.5}\text{MnO}_3$  [10]. Such doping of the Mn sites with a magnetic cation modifies the magnetic phase diagram of the manganites dramatically. The Mn-site doping with foreign cation can enhance FM exchange. It can also weaken and even destroy the charge ordering of  $\text{Mn}^{3+}$  and  $\text{Mn}^{4+}$  ions, which leads to formation of the AFM phase. Thus, the Mn-site doping can strongly influence the CMR properties resulting from the competition between FM metallic and AFM antiferromagnetic insulating domains [4,6,7,9,11].

Although a significant amount of papers, including Refs. [3–12], are devoted to the Mn-site doping in charge-ordered manganites, we are still far from understanding the role of dopant on the Mn site on the charge- and orbital-ordering processes. It is not clear which physical parameters of dopant ion are critical for maintaining or suppression of the charge- and orbitally-ordered states. Though it is established that charge ordering is accompanied by orbital ordering in  $\text{Ln}_{1-x}\text{A}_x\text{MnO}_3$ , the question whether orbital ordering influences charge ordering process or not is still open [13], and there are some reasons for this. First, most of the studies of Mn-site doping have been focused on the so-called ‘border’ compounds (with  $\text{Mn}^{3+}/\text{Mn}^{4+} = 1$ ), which are located on FM–AFM border in the phase diagram, where the phase separation is essential. This circumstance hinders understanding the effects of doping on charge ordering. Substitution of Mn can influence not only charge ordering itself, but can also affect the phase separation

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extent by increasing amount of the FM phase by formation of FM clusters, and this could be a crucial factor. In addition, in the case of the ‘border’ compounds, the introduction of a small amount of oxygen vacancies (that is rather typical for relatively high doping level [14]) could be critical and can mask the pure effect of Mn-site doping. Currently the systematic data on influence of the concentration and character of the dopants on charge ordering in the electron-doped  $\text{Ln}_{1-x}\text{A}_x\text{MnO}_3$  manganites ( $x > 0.50$ ) are missing. Therefore, for our study we have chosen  $\text{La}_{1/3}\text{Ca}_{2/3}\text{MnO}_3$  as the initial compound, where charge ordering dominates and the phase separation is negligible, since the FM fraction does not exceed 0.3% of the saturation value at low temperatures [15,16]. This allowed us to study effects of the Mn-site doping on the charge ordering transition in the ‘pure’ case. Our earlier experimental results have shown that substitution of Mn by magnetic  $\text{Fe}^{3+}$  [16],  $\text{Ni}^{2+}$  [17] and  $\text{Cu}^{2+}$  [18], as well as by diamagnetic  $\text{Ga}^{3+}$  [17], leads to a gradual decrease of  $T_{\text{CO}}$  with the dopant content  $y$ , with  $T_{\text{CO}}$  being proportional to the effective concentration of  $\text{Mn}^{3+}$  ions.

In this paper we have extended our study on influence of the Mn-site doping on the charge ordering transition to the elements Cr, Ru and Mg, and have demonstrated that the effect of doping on  $T_{\text{CO}}$  for  $\text{La}_{1/3}\text{Ca}_{2/3}\text{Mn}_{1-y}\text{M}_y\text{O}_3$  (Mn: Fe, Ga, Cr, Ni, Cu, Ru, and Mg) system exhibits a sort of universality. Namely, it has been shown for the first time that  $T_{\text{CO}}$  is governed by the effective relative concentration  $n_{\text{Mn}^{3+}} = \text{Mn}^{3+}/(\text{Mn}^{3+} + \text{Mn}^{4+})$  of  $\text{Mn}^{3+}$  ions,  $T_{\text{CO}} \sim C n_{\text{Mn}^{3+}}$ , where the coefficient  $C$  is the same for the dopant ions of the same valence (3+ or 2+), regardless of their  $d$ -shell filling. Universal behavior of  $T_{\text{CO}}$  with  $n_{\text{Mn}^{3+}}$  shows that any of the considered dopants does not participate in the charge ordering formation (however indirectly affects it), moreover, the orbital ordering does not affect  $T_{\text{CO}}$  in the doped manganites. On the basis of analysis of remanent magnetization behavior with dopant content and  $T_{\text{CO}}(n_{\text{Mn}^{3+}})$  dependences it has been concluded that the  $\text{Mn}^{3+}/\text{Mn}^{4+}$  ratio is responsible for AFM insulator–FM ‘bad’-metal phase transition observed in the Ru-doped system at  $y=0.07$ . Finally, the effect of Mn-site doping on  $T_{\text{CO}}$  has been considered in the framework of a simple theoretical model. According to the model, influence of the doping on  $T_{\text{CO}}$  is determined by changing degree of disorder accounted by the entropy rather than changing the energy. Qualitative agreement with the experiment has been obtained.

## 2. Experimental details

Polycrystalline samples were synthesized by solid state reaction similarly as was done in Refs. [16,17]. Initial materials  $\text{La}_2\text{O}_3$ ,  $\text{CaCO}_3$ ,  $\text{MnO}_2$  and appropriate oxide of dopant were mixed in stoichiometric proportions and heated twice in air at 900–1200 °C for 24 h with intermediate grindings. Cold forming was performed under a uniaxial pressure of 30 MPa. Conventional annealing was carried out at 1300 °C for 24 h in air.

The prepared samples were characterized by powder x-ray diffraction (XRD) using a Philips automated x-ray diffractometer with  $\text{Cu K}\alpha$  radiation. In addition, *in situ* in a scanning transmission electron microscope (STEM) JEOL 2010 F local (1–2 nm probe) compositional analysis was performed with a Princeton Gamma-Tech energy selective x-ray Si–Li analyzer (EDX) attached to the scanning transmission electronic microscope. Samples for the electron microscopy were thinned by mechanical polishing followed by argon ion milling down to electron transparency (< 50 nm).

Resistivity measurements were performed in the temperature range from 5 to 300 K with a standard four-probe method on  $2 \times 0.5 \times 8 \text{ mm}^3$  samples. The temperature dependence of the magnetization,  $M(T)$ , was measured in magnetic field  $H=1 \text{ T}$  in the temperature range 5–400 K with a commercial Quantum

Design SQUID magnetometer. The oxygen content in the studied samples was controlled by the iodometric titration method described, for example, in Ref. [14].

## 3. Results and discussions

### 3.1. Characterization of samples

Powder x-ray diffraction of all the studied compounds showed a single phase with perovskite structure ( $Pbnm$  space group) with  $a \approx b \approx \sqrt{2}a_p$  and  $c \approx 2a_p$  (where  $a_p \sim 3.9 \text{ \AA}$  is the lattice parameter of the simple perovskite structure [19]). No other phases or precipitates containing dopant atoms were revealed. Analysis of the XRD patterns showed that all the considered dopants do not change the lattice parameters significantly. The precise correspondence between the obtained chemical compositions and the nominal ones was checked by local EDX analysis with a fine probe of 1–2 nm diameter *in situ* in STEM. For this purpose we analyzed La:Ca:Mn:M ratio and distribution of dopant M in different positions within a separate grain and among not less than 20 different grains for each compound. The EDX analysis confirmed a good fit of the compositions to the nominal ones and very homogeneous distribution of the dopants in all the studied systems. Variation in the dopant content in different positions within a grain and among different grains did not exceed 5% from the nominal values, which is practically equal to the accuracy of the measurement. No dopant segregation at grain boundaries has been revealed for any dopants, except for Cu [18].

The iodometric titration analysis showed that the oxygen content in the samples with  $0 \leq y \leq 0.03$  is very close to the nominal value 3.0. For higher concentration of the dopants the oxygen content was slightly smaller (for example in Cu-doped samples with  $y \geq 0.04$  [18]), and this was taken into account for analysis of the experimental results. Some results of the iodometric titration for  $\text{La}_{1/3}\text{Ca}_{2/3}\text{Mn}_{1-y}\text{M}_y\text{O}_{3-\delta}$  ( $0 \leq y \leq 0.07$ ) systems are presented in Table 1.

A crucial problem in understanding the magnetic and electronic properties of the doped manganites is the valence of doping cations. Summary of the electronic structure of the dopants analyzed in our work is shown together with the ionic radii in Table 2. While Ga [17] and Mg enter  $\text{La}_{1/3}\text{Ca}_{2/3}\text{MnO}_3$  as the diamagnetic  $\text{Ga}^{3+}$  and  $\text{Mg}^{2+}$  ions, Ni ion in the parent compound

**Table 1**

Results of the iodometric titration for some  $\text{La}_{1/3}\text{Ca}_{2/3}\text{Mn}_{1-y}\text{M}_y\text{O}_{3-\delta}$  ( $0 \leq y \leq 0.07$ ) samples.

Dopant (M)	Dopant content (y)	Oxygen content (3- $\delta$ )
Fe	0.00	2.996
	0.04	2.993
	0.05	2.994
Ni	0.00	2.996
	0.015	2.998
	0.03	2.990
	0.07	2.957
Ga	0.00	2.996
	0.03	2.987
	0.05	2.950
Mg	0.00	2.996
	0.03	3.00
	0.05	2.993
Cu	0.00	2.995
	0.01	2.975
	0.04	2.97
	0.07	2.95

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