Impurity effect on orbital ordering and magnetic property in La$_{0.5}$Sr$_{1.5}$MnO$_4$

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Abstract. In this study we have investigated dopant effects on a typical charge-orbital ordered state in a single layered manganite La$_{0.5}$Sr$_{1.5}$MnO$_4$ using x-ray diffraction and magnetization measurement. We have studied how the orbital ordered states are affected by the 3% substitution of Cr, Fe and Ga ions for Mn ions. It is revealed that the orbital ordered states are suppressed by the magnetic impurities and the phase-separated state with charge-orbital ordering and ferromagnetic cluster and/or spin-cluster-glass state emerge in the all impurity doped compounds.

1. Introduction

Charge and orbital order (CO-OO) in mixed-valence manganites with perovskite-related structure has been attracting great interest since the CO-OO makes a strong impact on magnetism and electrical conduction, such as the colossal magneto-resistance (CMR) effect [1, 2]. In CO-OO system, in addition to the external field, quenched disorder arising from the local lattice distortion and/or doped impurities can also significantly modify the electronic structure. The effects of impurity doping on CO-OO perovskite manganites have been intensively investigated so far. For example, in a perovskite manganite Nd$_{0.4}$Ca$_{0.6}$MnO$_3$, the substitution of Cr ions for Mn ions immediately destroys the long-range CO-OO state and induces the ferromagnetic (FM) state locally, which results in the phase-separated ground state with both CO-OO and FM clusters randomly distributed [3]. In contrast to the Cr ion, Fe doping in CO-OO manganites gives a small influence; it leads only to the spin-glass-like insulating state without discernible FM transition [4]. Thus, the disorder effect on the CO-OO perovskite manganite is likely to significantly depend on the impurity species [5]. In this paper, we report the impurity effect on a single layered-manganite La$_{0.5}$Sr$_{1.3}$MnO$_4$ for a comparison with the effect on the perovskite manganites. In the two dimensional CO-OO system, the influence of impurity doping is expected to be limited only within the MnO$_2$ plane. The study focused on Cr$^{3+}$ (S = 3/2), Fe$^{5+}$ (S = 5/2) and Ga$^{3+}$ (S = 0) ions as doping impurities, which behave as not only magnetic but also orbital impurities because these ions don’t have orbital degrees of freedom.

The crystal space group of La$_{0.5}$Sr$_{1.3}$MnO$_4$ is I4/mmm with the tetragonal lattice constants $a = 3.86$ Å and $c = 12.44$ Å at room temperature. In La$_{0.5}$Sr$_{1.3}$MnO$_4$, nominal Mn$^{3+}$ and Mn$^{4+}$ sites are generated in a 1:1 ratio, and a checkerboard type charge ordered state appears below $T_{CO} = 230$ K. Upon this
transition, an orbital ordered state emerges concomitantly, where the $z^2-x^2$ and $y^2-z^2$ orbitals of the $e_g$ electrons line up in the manner as shown in figure 1(a). Actually such CO-OO pattern was determined by the resonant x-ray diffraction method [6]. The CO and OO are characterized by the wave vectors $(1/2 1/2 0)$ and $(1/4 1/4 0)$, respectively. The magnetic structure of pure compound is CE-type (see figure 1(a)) with the Néel temperature $T_N = 110$ K. In this study, the x-ray diffraction experiments and magnetization measurements in $\text{La}_{0.5}\text{Sr}_{1.5}\text{Mn}_{1-x}\text{M}_x\text{O}_4$ ($M = \text{Cr, Fe, and Ga}$) have been performed to clarify the doping effect on OO state and magnetic property.

2. Experiments

Single crystals of $\text{La}_{0.5}\text{Sr}_{1.5}\text{Mn}_{1-x}\text{M}_x\text{O}_4$ ($M = \text{Cr, Fe, and Ga}$) were grown using the floating zone method. The crystals oriented using XRD, and cut into thin plates with widest faces perpendicular to the [110] direction. Magnetization curves were measured using a superconducting quantum interference device magnetometer (Quantum Design). The single-crystal x-ray diffraction experiments with a four-circle diffractometer were performed using a rotating anode x-ray generator (XG) with a Mo target. In the experiments using XG, the incident x-ray energy was monochromatized to 17.44 keV (Mo Kα) by pyrolytic-graphite (0 0 2) monochromator. A closed-cycle He refrigerator was utilized to control the sample temperature. Superlattice diffraction associated with Jahn-Teller distortion characteristic of the CE-type OO appears at ($H/4, K/4, 0$) with $H, K = \text{odd and } H \neq K$. In this work, we performed longitudinal ($\theta$-2$\theta$) scans of the (1/4 7/4 0) reflections to measure the peak intensities and the full widths of half maximum (FWHM).

3. Results

Figure 1 shows the temperature dependences of (a) the intensities of $Q = (1/4 7/4 0)$ and (b) the FWHM for the $Q = (1/4 7/4 0)$ in $\text{La}_{0.5}\text{Sr}_{1.5}\text{Mn}_{1-x}\text{M}_x\text{O}_4$ ($x = 0.03$, $M = \text{Cr, Fe, and Ga}$). We measured the both (1/4 7/4 0) and (-1/4 7/4 0) reflections to estimate the actual intensity because there were two domains which have zigzag chains along [110] and [1-10], respectively, in CE-type OO. Here we plotted the intensities calculated with taking the domain ratio into account by these two
reflections. Although the intensities of all impurity doped compounds are increasing with decreasing temperature down to 10K as well as the pure compound, the transition temperatures are strongly suppressed by the impurity doping; the 3 % impurity doping effectively decreases $T_{CO}$ by about 20 K, 66 K, and 100 K, respectively for Ga, Cr, and Fe ions (the dopant dependence of $T_{CO}$ is summarized in figure 2 (b)). Though the concentration of impurity is common for all doped compounds, the OO transition temperature $T_{CO}$ vary with the dopant ions. The Cr and Fe doping also strongly suppress the intensities by about 50 % and 80 %, respectively. On the other hand, the same amount of Ga doping does not reduce the intensity at all. Although it seems that the intensity of Ga-doped compound is larger than that of pure compound, it would be not intrinsic feature of the doping but sample dependence. The correlation length $s$ estimated by the FWHM in Cr- and Ga-doped compounds are rarely different from that in the pure compound. Concerning the Fe-doped compound, the correlation length of OO seems to be shortened by about 10% but this reduction is attributed to the decrease of the overall lattice correlation length. Consequently, the few percentage magnetic impurity effectively weaken the OO state, however the correlation length is less affected by the impurity doping.

The magnetizations of $La_{0.5}Sr_{1.5}Mn_{1-x}M_{x}O_4$ were measured with applying a magnetic field of 0.1 T along the $a$-axis as shown in figure 2(a). Abrupt decreases in magnetization are seen at about 230 K and 210 K in pure and Ga-doped compound, respectively. The anomalies should correspond to the CO-OO transitions. In Cr- and Fe-doped compounds, the anomalies at the CO-OO transition temperatures seem to be weakened and weak magnetizations appear below ~80 K. The magnetizations increase down to the lowest temperature when the measurement after field cooling (FC), while broad peaks appear in the measurement after zero-field cooling (ZFC). A slightly difference in magnetization curve after FC and ZFC is also observed in the Ga-doped sample. Therefore the all doped crystals are assumed to undergo the transition to the phase-separated state with CO-OO and ferromagnetic (FM) clusters and/or spin-cluster-glass (SG) states. The temperatures which appear the differences of magnetizations between FC and ZFC are defined as the SG transition temperatures and are summarized in figure 2 (b).

However, the almost constant correlation lengths below $T_{CO}$ signal that the sizes of FM clusters would be very small. In the case of 3% impurity concentration, the average distance between impurities is about 23 Å within the MnO$_2$ planes (Mn-Mn length is 3.86 Å), therefore FM clusters are estimated to range over only several Mn sites around the impurity ions. Figure 3 presents the schematic pictures of CO-OO and magnetic structure for the doped compounds. Here we assume that the impurity ions are replaced with Mn$^{3+}$ ion. In the pure compound, the CE-type OO induces
the ferromagnetic coupling within the zigzag chain and the antiferromagnetic coupling between the zigzag chains. On the other hand, the magnetic interaction between impurity ions and neighbouring Mn\(^{4+}\) ions (3d\(^3\)) are supposed to be antiferromagnetic and ferromagnetic for Cr\(^{3+}\) ion (3d\(^3\)) and Fe\(^{3+}\) ion (3d\(^5\)), respectively. As shown in figure 3, the ferromagnetic spin configurations are preferred around the magnetic impurity ions for Cr- and Fe-doped compounds because the impurity ions have no orbital degree of freedom and are expected to have isotropic magnetic interactions with neighbouring Mn\(^{4+}\) ions. Thus the small FM clusters would be emerged on the impurity ions. In contrast, the Ga\(^{3+}\) ion (3d\(^{10}\)) is a non-magnetic impurity and has no magnetic interaction with the neighboring Mn\(^{4+}\) ions. Such a non-magnetic spin defects would induce the SG state around the Ga ions as observed in magnetization measurement.

4. Conclusion
In this study, we have investigated impurity effects on OO and magnetic property in La\(_{0.5}\)Sr\(_{1.5}\)MnO\(_4\). It is revealed that the transition temperatures \(T_{CO}\) decrease in all doped compounds and OO states are suppressed by the magnetic impurity ions. Temperature dependence of magnetization indicates that the phase-separated states with OO and FM cluster (and/or SG state) are emerged in all doped compounds. However the FM cluster would be limited to only several Mn sites around the impurity ions because the correlation lengths of OO do not shorten so much by the impurity doping.

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References
[1] M Imada, A Fujimori and Y Tokura 1998 Rev. Mod. Phys. 70 1039
[2] Y Tokura 2006 Rep. Prog. Phys. 69 797
[3] T Kimura, Y Tomioka, R Kumai, Y Okimoto and Y Tokura 1999 Phys. Rev. Lett. 83 3940
[4] A Machida, Y Moritomo, K Ohoyama, T Katsufuji and A Nakamura 2002 Phys. Rev. B 65 064435
[5] H Sakai, K Ito, T Nishiyama, X Yu, Y Matsu, S Miyasaka and Y Tokura 2008 J. Phys. Soc. Jpn. 77 124712
[6] Y Murakmi, H Kawada, H Kawata, M Tanaka, T Arima, Y Moritomo and Y Tokura 1998 Phys. Rev. Lett. 80 1932

Figure 3. Dopant variation of magnetic interaction between impurity ion and neighbouring Mn ions for (a) \(T = \text{Ga}\), (b) \(\text{Cr}\) and (c) \(\text{Fe}\) in La\(_{0.5}\)Sr\(_{1.5}\)Mn\(_{1-x}\)M\(_x\)O\(_4\).