Dependence of the Jahn-Teller distortion in LaMn$_{1-x}$Sc$_x$O$_3$ on the isovalent Mn-site substitution

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Abstract. We investigated the relative importance of removing the Mn$^{3+}$ Jahn-Teller distortion in driving ferromagnetism in LaMn$_{1-x}$Sc$_x$O$_3$ combining x-ray powder diffraction and x-ray absorption spectroscopy at the Mn and Sc K-edges. By increasing the Sc content, the orthorhombic distortion of the $Pbnm$ cell in LaMnO$_3$ decreases but the unit-cell remains slightly distorted in LaScO$_3$. Besides, the nearly tetragonal-distorted MO$_6$ in LaMnO$_3$ continuously evolves into a nearly regular one in LaScO$_3$. On the other hand, x-ray absorption spectra show that the MnO$_6$ octahedron remains Jahn-Teller distorted and the ScO$_6$ octahedron is nearly regular along the whole series. Moreover, the ordering of the Mn$^{3+}$ Jahn-Teller distortion is not disrupted in the ab plane for any Sc concentration. This contrasts with the Ga-substituted compounds, where a regular MnO$_6$ is found for x>0.5. However, both LaMn$_{0.5}$Sc$_0.5$O$_3$ and LaMn$_{0.5}$Ga$_0.5$O$_3$ show ferromagnetic behavior independently of the presence (or not) of Jahn-Teller distorted Mn$^{3+}$. Thus, our results point to the Mn-sublattice dilution as the main effect in driving ferromagnetism in these manganites over local structure effects previously proposed by the spin flipping or the vibronic superexchange models.

1. Introduction

Doped manganites have been extensively studied owing to their colossal magnetoresistance property and its potential applications to magnetic devices. In particular, LaMnO$_3$ is considered as the prototype of the cooperative Jahn-Teller (JT) systems and orbital-ordered state [1]. It also develops long-range antiferromagnetic (AFM) ordering of type A below $T_N$=140 K. The substitution at the Mn dramatically modifies the magnetic and electronic properties. It is known that the A-type AFM orbitally ordered state of LaMnO$_3$ is easily destroyed to give way to ferromagnetism (FM) by introducing various cations on the Mn site [2-5]. However, this ferromagnetic behavior derives from a complex interplay between several mechanisms: double-exchange and super-exchange interactions, orbital order and JT distortions. The substitution of Mn with non-magnetic isovalent ions such as Ga$^{3+}$ (3d$^{10}$) or Sc$^{3+}$ (3d$^1$) weakens the Mn$^{3+}$-Mn$^{3+}$ super-exchange interactions but surprisingly favors the appearance of a FM ground state for LaMn$_{0.5}$Ga$_0.5$O$_3$ [3,4] and LaMn$_{0.5}$Sc$_0.5$O$_3$ [5]. Two models have been reported to account for this property: the spin flipping of Mn e$_g$-orbital in JT-distorted Mn$^{3+}$ atoms surrounded by...
Ga (Sc) atoms [6] and the FM vibronic superexchange interaction coming from disordered and fluctuating JT-distorted Mn\(^{3+}\) atoms [7]. Both models assume that the change from A-type AFM to FM ordering is originated by the orbital direction adopted by the Mn\(^{3+}\) ion and it is similar for Ga and Sc non-magnetic substitutions, so the atomic e\(_g\) orbital would be perturbed in the same way for the two series.

These models contrast with previous x-ray absorption spectroscopy (XAS) studies [8-10]. A XAS study of the LaMn\(_{1-x}\)Ga\(_x\)O\(_3\) series have revealed that the tetragonal distortion of MnO\(_6\) octahedron continuously decreases with the gallium content in such a way that for x>0.5 MnO\(_6\) distortion disappears and becomes regular [8,9], simultaneously to the appearance of long-range FM. Moreover, a XAS study of the isostructural TbMn\(_{1-x}\)Sc\(_x\)O\(_3\) series showed that the MnO\(_6\) octahedra remain tetragonally distorted along the whole dilution range, independently of the Sc content [10].

Here, we have studied the crystallographic structure by x-ray powder diffraction (XRD) and the local structure by XAS at the Mn and Sc K-edges in the LaMn\(_{1-x}\)Sc\(_x\)O\(_3\) series in order to clarify the importance of removing the Jahn-Teller distortion in driving the FM behavior.

2. Experimental details

Powder LaMn\(_{1-x}\)Sc\(_x\)O\(_3\) (x = 0, 0.1, 0.2, 0.3, 0.4, 0.5, 0.6, 0.7, 0.9, 1) samples were synthesized following the same ceramic procedure as previously outlined for LaMn\(_{1-x}\)Ga\(_x\)O\(_3\) [3]. XRD patterns were collected for the whole series in the 2-theta range between 18\(^\circ\) and 135\(^\circ\) at room temperature by using a D-max Rigaku system with a rotating anode and selecting the Cu K\(_{\alpha}\) radiation. The crystal structures were refined by the Rietveld method using the program FULLPROF [11].

The Mn K-edge XAS spectra were recorded at the BM23 beamline of the European Synchrotron Radiation Facility. Data were recorded at a fixed T~80 K in transmission mode for Sc concentration up to x=0.6 while for higher dilutions fluorescence detection was used. The Sc K-edge XAS measurements were carried out at fixed temperature at the CLAESS beamline of the ALBA synchrotron for Sc concentration x>0.3 whereas temperature-dependent XAS spectra of the LaMn\(_{0.4}\)Sc\(_{0.6}\)O\(_3\) sample were collected at the XAFS beamline of the Elettra Synchrotron. Data for x>0.4 were recorded in transmission mode while for lower Sc concentration fluorescence detection was used. XANES spectra were normalized to unity edge jump using the Athena software from the Demeter package [12]. The extraction of the \(\chi(k)\) signals were also performed using Athena program, and R-space EXAFS spectra were obtained by calculating the Fourier Transform (FT) of the \(k^2\chi(k)\) signals in the (2.5-14) \(\text{Å}^{-1}\) k-range. The EXAFS structural analysis was performed using theoretical phases and amplitudes calculated by the FEFF-6 code [13] and fits to the experimental data were carried out in R-space with the Artemis program of the Demeter package [12].

3. Results and conclusions

The XRD results show that the tetragonal distortion of the MO\(_6\) octahedron continuously decreases with the Sc content (figure 1). There are two possibilities that could explain this fact: either both MnO\(_6\) and ScO\(_6\) octahedron are equally distorted, and the magnitude of the correlated distortion decreases with x, or the observed distortion of MO\(_6\) by XRD corresponds to the average of different MnO\(_6\) and ScO\(_6\) octahedra. In figure 1, we have compared the M-O distances from XRD with the weighted addition of the Mn-O and Sc-O distances taken from XRD for the end-member compounds of the series, LaMnO\(_3\) and LaScO\(_3\). The same comparison was also made with the weighted addition of the Mn-O and Ga-O distances for the LaMn\(_{1-x}\)Ga\(_x\)O\(_3\) series as reported in the inset of figure 1. The agreement is very good, which means that the geometrical orientation of the MnO\(_6\) tetragonal distortion is preserved in the ab plane in both, Sc-substituted and Ga-substituted compounds.

In the Ga-substituted samples, different MnO\(_6\) and GaO\(_6\) octahedra are deduced by XAS where the JT-distortion of the Mn\(^{3+}\)O\(_6\) decreases with the Ga substitution and the appearing of FM concurs with the presence of regular Mn\(^{3+}\)O\(_6\) octahedron (x>0.5). The occurrence of Mn tetragonal distortions, which remain ordered even up to high Sc content, has been also reported for the TbMn\(_{1-x}\)Sc\(_x\)O\(_3\) series [10].
Figure 1. Evolution with the Sc content of the MO$_6$ octahedron (closed symbols) compared to the weighted addition of the M-O distances of the two end-member LaMnO$_3$ and LaScO$_3$ (lines) from XRD. Inset: same comparison for the LaMn$_{1-x}$Ga$_x$O$_3$ series.

No edge energy shift is observed between the LaMn$_{1-x}$Sc$_x$O$_3$ samples and either the LaMnO$_3$ sample at the Mn K-edge or the LaScO$_3$ sample at the Sc K-edge (figure 2) within the precision of the experiments (0.4 eV). Thus, Mn$^{3+}$ formal valence keeps constant along the dilution.

Figure 2. Left. Normalized Mn K-edge XANES spectra of LaMn$_{1-x}$Sc$_x$O$_3$ (x=0, 0.9). Right. Normalized Sc K-edge XANES spectra of LaMn$_{1-x}$Sc$_x$O$_3$ (x=0.3, 1).

Figure 3 shows the modulus of the FT of the $k^2$-weighted EXAFS signals of selected concentrations of Sc. All samples show a main peak at ~1.5 Å (Mn K-edge) and ~1.6 Å (Sc K-edge) corresponding to the first (Mn-O or Sc-O) coordination shell without phase shift correction. The intensity and shape of this peak is practically independent of the dilution indicating that the oxygen coordination geometry around both, Mn and Sc atoms, remains almost unaltered along the whole series. The structural analysis at the Mn K-edge was performed considering the same shift on the equatorial plane (Mn-O$_1$short and Mn-O$_2$short, delr$_1$) and a different one for the apical distances (Mn-O$_2$long, delr$_2$) of the MnO$_6$ octahedron. The relevant structural parameters for the first oxygen coordination shell of all samples are shown in the inset of figure 3 (left). The same tetragonal distorted (JT) MnO$_6$ as in LaMnO$_3$ is found for all Sc substitutions. At the Sc K-edge, we have performed the fits considering the three pairs of Sc-O distances slightly distorted of LaScO$_3$ but they converge to a unique distance. As shown in the inset of figure 3 (right), the same nearly regular ScO$_6$ octahedron as in LaScO$_3$ is found for all Sc concentrations. The temperature-dependent EXAFS spectra of LaMn$_{0.4}$Sc$_{0.6}$O$_3$ at the Mn and Sc K-edges between 80 and 300 K confirm the robustness of MnO$_6$ tetragonal distortion and the lack of significant static distortion of ScO$_6$ for LaMn$_{0.4}$Sc$_{0.6}$O$_3$ along this temperature range.
The present results show a marked difference in the local structure for LaMn$_{1-x}$Ga$_x$O$_3$ and LaMn$_{1-x}$Sc$_x$O$_3$. MnO$_6$ is hardly distorted in an environment composed by regular GaO$_6$ octahedra whereas this distortion results more feasible when MnO$_6$ is surrounded by ScO$_6$ octahedra because of the larger tilts of the ScO$_6$ octahedron in the orthorhombic Pbnm cell. Therefore, the occurrence of the tetragonal distortion of the MnO$_6$ octahedron strongly depends on the lattice in which Mn atom is allocated. Despite the different structural behaviour found for Ga and Sc substitutions, the magnetic response for $x \geq 0.5$ is similar in both cases. The two proposed models [6,7] to account for the change from A-type AFM to FM cannot be supported by either the present structural study or that in the Ga-substituted samples [8,9] so the Mn-sublattice dilution effect may be the main responsible for the magnetic behaviour of these manganites.

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