XAS study of Ru doped $n = 1, 2$ Ruddlesden–Popper manganites

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Abstract

We report on the results of X-ray absorption near edge structure (XANES) studies at the Mn:$L_{2,3}$, Ru:K and O:K edges of novel manganites, $Sr_2Mn_{0.5}Ru_{0.5}O_4$ and Sr_3MnRuO_7. Measurements were carried out on polycrystalline powder samples at room temperature. From the analysis of the XANES spectra the average manganese valences of 3.4 in bilayer Sr_3MnRuO_7 and 3.1 in single layer $Sr_2Mn_{0.5}Ru_{0.5}O_4$ are obtained. The corresponding average valences for Ru ions are 4.6 and 4.9, respectively. This indicates that Ru doping gives rise to a decrease of Mn valence, whereas Ru valence increases, compared to Mn(IV) and Ru(IV) in undoped compounds. The effect of charge disproportionation is stronger in the single layered compound than in the bilayered one.
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Nowadays, there is a continuous search for new magnetoresistive materials that are potential candidates for applications in spin valves, field sensing and data storage devices [1,2]. The most common 'colossal' magnetoresistive materials, studied over the past decade, are those of 'three dimensional' mixed valence manganites of perovskite structure. Recently, layered Ruddlesden–Popper (RP) structures such as Sr_3MnRuO_7 and $Sr_2Mn_{0.5}Ru_{0.5}O_4$ [3] have been also shown to exhibit magnetoresistive properties. The Ru doped manganites, $Sr_2Mn_{0.5}Ru_{0.5}O_4$ and Sr_3MnRuO_7, represent the $n = 1$ and 2 families of RP oxides, $A_{n+1}B_nO_{3n+1}$, respectively. The interest in mixed Ru/Mn RP phases was stimulated by observation that low concentration of Ru doping of charge ordered $n = \infty$ (perovskite) manganites can induce ferromagnetism and metallicity [4]. Nevertheless, neither of studied RP phases shows long-range magnetic order at low temperatures, but spin glass behavior below 16 K ($n = 1$) or 25 K ($n = 2$). They also have a maxi-

mum magnetoresistance (MR) of ∼8% in 14 T at temperatures between 50 and 70 K [3].

One crucial problem in understanding the magnetic and electronic properties in manganites, especially in doped compounds, is that of the valence of Mn and doped transition element cations. In order to shed some light on this problem, XAS (X-ray absorption spectroscopy) studies in the XANES range were carried out. The absorption of X-ray quanta results in the excitation of a core electron into unoccupied states above the Fermi level. For the K ($L_{2,3}$) edge the absorption coefficient in the vicinity of the absorption edge is roughly proportional to the density of p-type (d-type) unoccupied states. Therefore, XAS spectra can be regarded as fingerprints of different valence states of elements, in particular Mn, in solids [5–8].

Most XAS results presented in this paper are based on the measurements at the Mn:$L_{2,3}$ and O:K edges, which were carried out on the BACH beamline in ELETTRA, Trieste, Italy. Powder samples of Sr_3MnRuO_7 and $Sr_2Mn_{0.5}Ru_{0.5}O_4$ were measured at room temperature by means of TEY (total electron yield) detection techniqe. The Mn_2O_3 and $MnO_{2-\gamma}$ (exact stoichiometry $MnO_{1.9}$), samples were used as Mn(III) and Mn(IV)

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references, respectively. Powders of the compounds and the reference samples were glued to a conductive tape attached to the molybdenum foil, which was fixed at the sample holder. XAS measurements at the Ru:K edge were carried out at the station A1 of Hasylab/DESY, Hamburg, Germany. The spectra were measured in transmission mode at room temperature using the four crystal Si(3 1 1) monochromator. Samples of La_2NiRuO_6 and Ba_2LaRuO_6 were used as references for Ru(IV) and Ru(V), respectively [9,10].

Atomic multiplet calculations [11] have shown that the Mn valence state has more influence on the shape of the $L_{2,3}$ XANES spectra than on the edge position, in contrast to the K edge XANES spectra, where the valence state influences mainly the edge energy and the shape is predominantly determined by the symmetry of the local environment [12]. Therefore, in order to determine the average Mn valence state in the compounds studied from the $L_{2,3}$ XANES spectra, they were reproduced by a weighted sum of the Mn(III) and Mn(IV) reference spectra. One should note that the crystal field can strongly affects the shape of the Mn:$L_{2,3}$ edges, which can have impact on the determination of the average Mn valence. Since the distortions of Mn octahedra are similar in both RP compounds, we assume that the XANES spectra are determined mostly by the density of unoccupied Mn 3d states. It is also worth noting that the measured Mn:$L_{2,3}$ edges of Mn_2O_3 and $MnO_{1.9}$ presented in Fig. 1
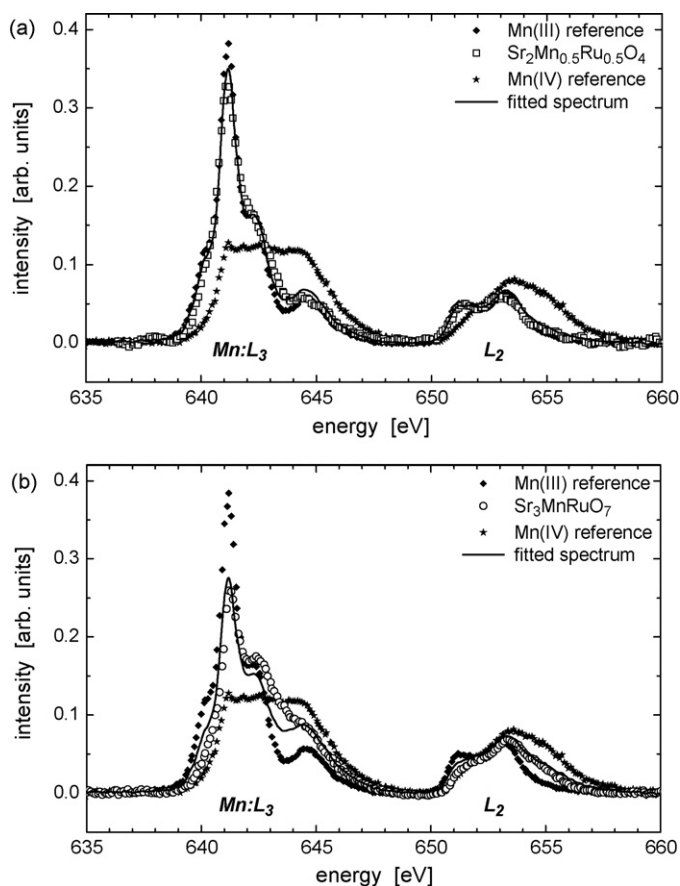

Fig. 1. (a) Mn:$L_{2,3}$ edge spectra of $Sr_2Mn_{0.5}Ru_{0.5}O_4$ with references; (b) Mn:$L_{2,3}$ edge spectra of Sr_3MnRuO_7 with references. The black line, in each plot, is the fit to the data as explained in the text.

as Mn(III) and Mn(IV) references, respectively, show slightly different shape from those obtained in theoretical calculations [12] and previous experiments [13–15]. Despite the fact that the spectra presented in ref. [13] represent a much higher experimental resolution of 0.15 eV than that in our experiment, which was estimated at 0.35 eV, a general similarity can be found.

In order to determine the Mn valence from the Mn:$L_{2,3}$ XAS spectra, the following analysis was carried out. The edge step background was removed using arctan functions subtracted from the raw Mn:$L_{2,3}$ spectra and the area under the edge peaks was normalized to unity for all the spectra, including the Mn(III) and Mn(IV) references. Such a normalization provides a more reliable relation of the spectra to the DOS per absorbing atom than that of the edge step method, since the $L_{2,3}$ edge steps are small and difficult to determine accurately from the spectra dominated by the white line features.

For Ru:K edge, empty 5p states are probed and the valence state can be determined from the edge energy compared to the corresponding edge energies of the Ru(IV) (22134.1 eV) and Ru(V) (22135.5 eV) references. Conventionally, one determines the energy of the K edge by taking the first derivative of the experimental data. However, due to a substantial statistical noise of the spectra the edge energies were derived from a third order polynomial fit in the region of intensities of 0.2–0.8 of the edge step normalized spectra and the energy corresponding to the inflection point of the polynomial was determined as the edge position. In the average valence estimation procedure the energy of the absorption edge was assumed as linearly dependent on the average valence state.

The Mn:$L_{2,3}$ edge XAS spectra for $n = 1$ and 2 Ruddlesden–Popper Ru doped manganites are shown in Fig. 1a and b. From the fits presented, the average valence of Mn in Sr_3MnRuO_7 of 3.42(5) is obtained. Consequently, the average Ru valence of 4.58(5) is derived. For $Sr_2Mn_{0.5}Ru_{0.5}O_4$, the Mn and Ru average valences are 3.08(5) and 4.92(5), respectively. As the parent $Sr_3Mn_2O_7$ and $Sr_3Ru_2O_7$ as well as Sr_2MnO_4 and Sr_2RuO_4 compounds are in the Mn(IV) and Ru(IV) oxidation states, the results clearly show that the substitution of Mn with Ru gives rise to a decrease of the average Mn valence and corresponding increase of the average Ru valence. This effect of charge disproportionation is larger in the single layer compound than in the bilayer one.

The O:K edge, Fig. 2, shows that for $Sr_2Mn_{0.5}Ru_{0.5}O_4$ and Sr_3MnRuO_7, the absorption at the edge step and the post-edge structure is similar. For Sr_3MnRuO_7 a pre-edge feature is observed, which energy coincides with that of $MnO_{2-\gamma}$. This suggests that manganese in this compound has a higher oxidation state than in $Sr_2Mn_{0.5}Ru_{0.5}O_4$, which is consistent with Mn:$L_{2,3}$ edge results. Extra features at higher energies may be due to multi-electronic excitations and from multiple scattering of the photo-excited electron on the neighbouring atoms.

The edge steps in the Ru:K edge spectra of the $n = 1$ and $n = 2$ compounds, Fig. 3, correspond to different energies. Assuming a linear relation between the valence and edge energy, the Ru valences for $Sr_2Mn_{0.5}Ru_{0.5}O_4$ and Sr_3MnRuO_7 of 4.9(2) and 4.6(2) are obtained, respectively. Consequently, the average Mn valence of 3.1(2) for $Sr_2Mn_{0.5}Ru_{0.5}O_4$ and 3.4(2) for
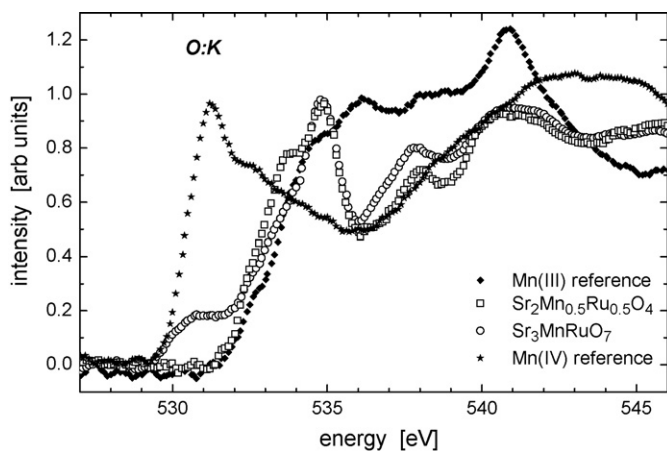
Fig. 2. O:K edge spectra of $Sr_2Mn_{0.5}Ru_{0.5}O_4$ and Sr_3MnRuO_7 with reference samples for Mn(III) and Mn(IV) (stars).
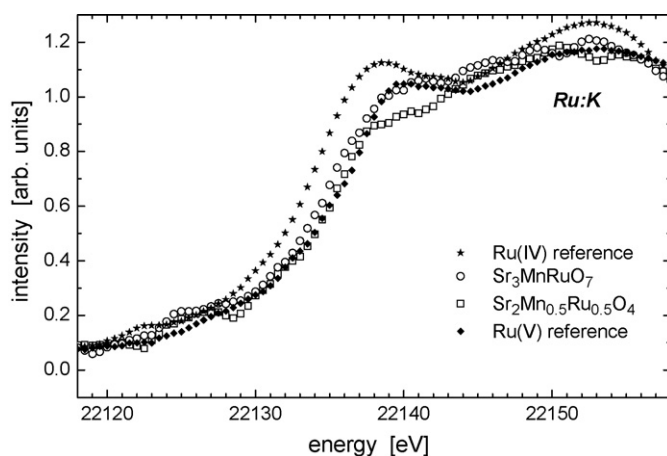
Fig. 3. The Ru:K edge spectra of $Sr_2Mn_{0.5}Ru_{0.5}O_4$ and Sr_3MnRuO_7 with reference samples.

Sr_3MnRuO_7 is deduced. This agrees within the error margin with the average valences obtained from the Mn:$L_{2,3}$ edges spectra.

In conclusion, the XAS measurements on the selected RP compounds presented in this work have provided the information on the average Mn and Ru valence states in substituted compounds. For both compounds, Sr_3MnRuO_7 and $Sr_2Mn_{0.5}Ru_{0.5}O_4$, substitution of Mn with Ru leads to a decrease of Mn valence and an increase of Ru valence compared to their parent compounds. A difference in Mn and Ru valence states is observed in the single layered compound compared to the bilayered compound which might suggest that there is extra freedom of the axial oxygen in the $n = 1$ structure, which allows it to relax into the rock salt-like layer, stabilizing to a higher Mn(III) concentration.

Acknowledgements

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