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# Determination of manganese valency in $La_{1-x}Sr_xMnO_3$ using ELNES in the (S)TEM

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## Abstract

In this article several experimentally identified Mn valence-sensitive ELNES quantities for the $La_{1-x}Sr_xMnO_3$ compound class are presented, namely the energy separations between Mn-$L_3$ and O-$K_a$, between O-$K_b$ and O-$K_a$ edges, the Mn-$L_{2,3}$ white line intensity ratio, and the Mn-$L_3$ line width. Valence sensitivities of these quantities are evaluated, and possible additional influences on them are considered. At high signal-to-noise ratio the two energy separations display most sensitively changes of the Mn valency. An experiment-based estimation of the total uncertainties of the quantities indicates that at low signal-to-noise ratio, which is the case when studying interface effects at high spatial resolution, again both energy separations allow to resolve the smallest valency changes.

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*Keywords:* ELNES; EELS; Valence sensitivity; White line; $La_{1-x}Sr_xMnO_3$

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## 1. Introduction

The analysis of electron energy-loss near edge structures (ELNES) in the (scanning) transmission electron microscope ((S)TEM) offers the possibility to obtain information on electronic structure and chemical bonding at high spatial resolution. In case of single-scattering core-loss edges the intensity in the ELNES region, which extends up to 50 eV above the edge threshold, probes the local, symmetry-projected density of unoccupied states near the Fermi level (Egerton, 1996). In the late 1980s and early 1990s several studies on Mn oxides were published which relate the Mn valency to the Mn-$L_{2,3}$ white line intensities and to the energy positions of O-K and Mn-$L_{2,3}$ edges (Sparrow et al., 1984; Rask et al., 1987; Pearson et al., 1988, 1993; Paterson and Krivanek, 1990; Kurata and Colliex, 1993). In the late 1990s the interest in valency determination, particularly at high spatial resolution has been renewed, since the Mn oxidation state in thin colossal magnetoresistance manganite films turned out to considerably influence the performance of corresponding magnetoelectronic devices (Noh et al., 2001).

In this context it is valuable to know the suitability of different ELNES measures for the quantitative determination of Mn valency in $La_{1-x}Sr_xMnO_3$. The $La_{1-x}Sr_xMnO_3$ compound class has been chosen, since $La_{0.7}Sr_{0.3}MnO_3$ (LSMO) exhibits half-metallic properties with nearly total spin polarization (Bowen et al., 2003) and has the highest Curie temperature (370 K) among manganites (Dagotto et al., 2001) making it attractive for room temperature applications such as magnetoresistive tunnel junctions (Sun et al., 1997). In thin film devices the Mn valency is influenced by several factors like local composition, strain, magnetic structure and phase segregation, which are often governed by the substrate-film or film–film misfits. For an accurate valency determination in manganite films sensitive measures are required. Since experimental studies (Horiba et al., 2005) and calculations (Banach and Temmerman, 2004) confirm that the mean Mn valency in bulk $La_{1-x}Sr_xMnO_3$ varies monotonously with Sr doping $x$, bulk reference samples of this material seem to be suitable for studying valence-induced ELNES changes.

The article is organized as follows: after describing the experimental details in Section 2, Section 3 gives an overview of various Mn valence-dependent ELNES quantities with

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emphasis on their valence sensitivity. Section 4 applies these ELNES quantities to thin LSMO films and estimates their valence sensitivities for a broad range of signal-to-noise ratios (SNR). Finally, Section 5 draws conclusions.

## 2. Experiment

Powder-like $La_{1-x}Sr_xMnO_3$ reference samples with $x = 0.2$, 0.4, and 0.7 were synthesized by the solid state reaction method (Oseroff et al., 1996; Proffen et al., 1999). Starting materials consisted of $La_2O_3$(MaTeck, 99.99% purity), $Mn_2O_3$(ChemPur, 99.9% purity), and $SrCO_3$ (Merck, 99.9% purity). The chemical composition of the products was checked: Lanthanum, strontium and manganese were determined by inductively coupled plasma optical emission spectroscopy, oxygen by carrier gas hot extraction (Gruner, 1999). In addition, the presence of phases of nominal composition was confirmed by X-ray diffraction. The compounds were then prepared for TEM. Small, electron transparent regions were obtained by grinding and dispersing the powder in ethanol using ultrasound. For the determination of the influence of TEM specimen thickness on the ELNES an LSMO film of ≈ 60 nm thickness was deposited on $SrTiO_3(0\ 0\ 1)$ substrate (both single-crystalline) by off-axis pulsed laser deposition (Holzapfel et al., 1992). Cross-sections were prepared for TEM by dimple grinding followed by ion milling at 4 keV initial and 0.5 keV final ion energies. All specimens were then investigated in STEM mode in an analytical TEM (Tecnai F 30, FEI) equipped with an imaging energy filter (GIF 200, Gatan) at 300 kV. Zero-loss as well as O-K and Mn-$L_{2,3}$ core-loss spectra of ≈ 100 $nm^2$ specimen regions were recorded (Fig. 1). For the applied doses electron beam stability of the examined Mn oxides could be confirmed. Since the Mn white lines $L_3$ and $L_2$ are well separated in energy, their distinction does not require high energy resolution. To obtain high edge intensities we selected specific gun settings and a spectrometer entrance aperture of 2 mm resulting in standard energy resolution for our system of 1.6 eV and a collection semi-angle of 6 mrad. Specimen thicknesses of the reference samples ranged between 0.22 and 0.85 mean free path lengths ($\lambda$) for inelastic scattering. Furthermore, the La:O and Mn:O atomic ratios were checked. All spectra were dark-current and gain corrected.

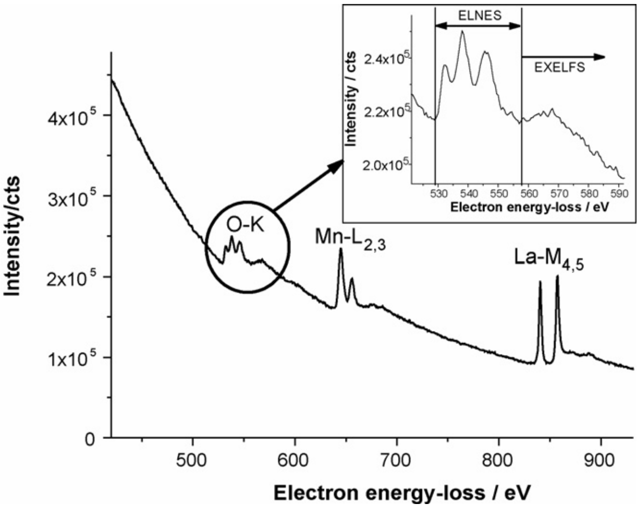

Fig. 1. Electron energy-loss spectrum of the $La_{0.6}Sr_{0.4}MnO_3$ reference sample with O-K and Mn-$L_{2,3}$ edges.

## 3. Mn valence-sensitive ELNES quantities

To study the Mn valence-induced ELNES changes measured O-K and Mn-$L_{2,3}$ electron energy-loss (EEL) edges of the three $La_{1-x}Sr_xMnO_3$ reference samples were compared. These changes were quantified in different characteristic measures $Q$, which will be analyzed in the following subsections:

- Mn-$L_{2,3}$ white line intensity ratio;
- energy separations between Mn-$L_3$ and O-$K_a$, and between O-$K_b$ and O-$K_a$ edges;
- Mn-$L_3$ line width.

For the determination of the valence sensitivity of each $Q$ we have estimated the Mn valency of each $La_{1-x}Sr_xMnO_3$ sample using the obtained chemical compositions displayed in Table 1. Within the relative standard deviations of 0.2–0.4% they reveal minor deviations from the nominal compositions. Relative to Sr and Mn, La is in excess (by ≈ 1%) for all samples, whereas O

Table 1
$La_{1-x}Sr_xMnO_3$ reference samples: chemical composition (upper part); stoichiometry and Mn valency (Eqs. (3) and (4)) calculated from chemical analysis results (lower part)

| Sample | La content (mass%) | Sr content (mass%) | Mn content (mass%) | O content (mass%) | $\sum$ (La, Sr, Mn, O) (mass%) |
|---|---|---|---|---|---|
| $La_{0.8}Sr_{0.2}MnO_3$ | 47.96 | 7.49 | 23.46 | 20.61 | 99.52 |
| $La_{0.6}Sr_{0.4}MnO_3$ | 37.85 | 15.71 | 24.72 | 21.25 | 99.53 |
| $La_{0.3}Sr_{0.7}MnO_3$ | 20.34 | 29.63 | 26.61 | 22.79 | 99.37 |

| Sample | Found stoichiometry | Nominal Mn valency (vu) | Found Mn valency (vu) |
|---|---|---|---|
| $La_{0.8}Sr_{0.2}MnO_3$ | $La_{0.808}Sr_{0.200}Mn_{0.999}\ O_{3.014}$ | 3.2 | 3.20 ± 0.04 |
| $La_{0.6}Sr_{0.4}MnO_3$ | $La_{0.608}Sr_{0.400}Mn_{1.004}\ O_{2.963}$ | 3.4 | 3.30 ± 0.04 |
| $La_{0.3}Sr_{0.7}MnO_3$ | $La_{0.303}Sr_{0.700}Mn_{1.003}\ O_{2.949}$ | 3.7 | 3.59 ± 0.03 |

The Sr stoichiometry coefficients were preset to the nominal values. vu denotes the valency unit.