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Extraction of EELS white-line intensities of manganese compounds: Methods, accuracy, and valence sensitivity

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Abstract

This article evaluates the valence sensitivity and accuracy of selected EELS white-line extraction methods based on the white-line intensity ratio in case of manganese oxides, predominantly in the valency range [Mn^{3+}; Mn^{4+}]. For this purpose Mn–$L_{2,3}$ ionization edges of several Mn oxides were measured and four different methods were applied to extract the intensities. The obtained ratios have been analyzed in terms of their errors, their scatter, and their sensitivity on manganese valency. We found that the maximum-intensity as well as the Pearson and Walsh–Dray methods show larger relative changes of the ratio between Mn^{3+} and Mn^{4+} than curve-fitting. Taking the scatter into account, Walsh–Dray distinguishes more clearly between those two valencies than curve-fitting. Thus the Walsh–Dray method promises the most accurate determination of small valency shifts.

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Keywords: EELS; White-line; Extraction method; Valence sensitivity; Accuracy

1. Introduction

Electron energy-loss spectroscopy (EELS) white-lines (WL) of first row transition metals contain rich information about the density of unoccupied states near the Fermi level and the chemical bonding of the metal [1,2]. WL are pronounced, sharp peaks occurring near the onset of transition metal $L_{2,3}$ edges in the energy-loss spectrum. The L_3 and L_2 lines correspond to electron transitions from $2p_{3/2}$ and $2p_{1/2}$ core states to bound unoccupied 3d states, respectively [3], which hybridize with oxygen 2p orbitals in the case of oxides. The continuous background below the WL arises from transitions to continuum states. Each of the L_3 and L_2 peaks has its distinctive fine structure caused by atomic effects [4]. The two lines are separated by the spin–orbit interaction of the 2p core states which amounts to about 11 eV for Mn [5]. From the $(2j+1)$ degeneracy of the initial $2p_j$ ($j=\frac{3}{2},\frac{1}{2}$) states, i.e. four $2p_{3/2}$ electrons and two $2p_{1/2}$ electrons, one expects a WL intensity ratio of 2 [6]. However, for some 3d transition metals and their oxides anomalously high ratios were found [7]. Obviously the ratio relates to the occupancy of 3d orbitals with a maximum value for a $3d^5$ configuration and decreases towards $3d^0$ and $3d^{10}$. This behavior can be understood by spin–spin coupling determining the L_3, L_2 transition probabilities [8] as confirmed by atomic multiplet calculations [9,10]. Consequently, the WL ratio can be used to measure the transition metal valency. Other authors emphasize that also the sum of the WL intensities divided by the continuum contribution is suitable for valency determination, since it correlates linearly with the effective 3d occupancy [6,11]. However, the difference in this normalized total WL intensity between Mn_2O_3 and MnO_2 is very small leading to a low valence sensitivity. Therefore, only the WL ratio is considered here. Before retrieving the valency the WL have to be isolated from the raw spectrum. In the past several approaches were pursued to extract the intensities. Pearson et al. [12] recognized the necessity to subtract the continuum intensity. Later on hydrogenic and Hartree–Slater models were adopted to match the continuum contribution more accurately [13].

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Moreover, parameter models were established and fitted to the core-edge region. Further on, some refinements regarding the background subtraction, the continuum fit and the integration intervals were introduced [11,14]. Furthermore, Co and Mn WL were used to map the lateral distribution of cation valence states by means of energy filtered transmission electron microscopy [15].

In this work we focus on Mn, because recently advances have been made in the development of manganite based magnetoelectronic devices [16,17]. There are strong indications that disorder in the atomistic and electronic (in particular the valency) structure [18,19] near interfaces in manganite thin film tunnel junctions considerably reduces spin polarization [20], effective Curie temperature [21] and hence their performance. In this context Mn valency determination has gained importance.

After describing the experimental details in Section 2, Section 3 summarizes the selected WL extraction methods. Section 4 discusses various error sources for each method. The determined WL intensity ratios with focus on valence sensitivity of the extraction methods are presented in Section 5. Finally, Section 6 draws conclusions reflecting on the main results.

2. Experiment

Three manganese oxides, namely Mn_2O_3, MnO_2, and $BaMnO_4$ (Table 1) were prepared from powder-like raw material for transmission electron microscopy (TEM). Small, electron transparent regions were obtained by dispersing the powder via ultrasound. The specimens were investigated in an analytical TEM (Tecnai F30, FEI) in STEM mode equipped with an imaging energy filter (GIF200, Gatan) at 300 kV. Zero-loss and core-loss energy-loss spectra of 100 nm^2 specimen regions were recorded. For the applied doses electron beam stability of the examined Mn oxides could be confirmed. Since the Mn WL L_3 and L_2 are well separated in energy, their distinction does not require high energy resolution. To obtain sufficient edge intensity we selected 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. Signal-to-noise ratios (SNR) of ≈ 170 were achieved. Specimen thicknesses ranged between 0.1 and 0.3 mean free path lengths for inelastic scattering, therefore a deconvolution of plural scattering was not applied. Furthermore, the Mn:O atomic ratios of all acquired spectra were checked to ensure practically constant Mn:O composition for the compared spectra of each compound. All spectra were dark-current and gain corrected.

Table 1
Analyzed materials, their structures and sources

Compound	Mn valency	Structure type	Space group	Source
Mn_2O_3	+3	Bixbyite	Ia3	Pharmacie Centrale de France
MnO_2	+4	Rutile	$P\frac{4}{m}nm$	VEB Berlin GmbH
$BaMnO_4$	+6	–	Pbnm	ABCR GmbH

3. Extraction methods of white-line intensities

Following the subtraction of a power-law background by means of the DigitalMicrograph software [22] four different methods to extract the WL intensities from the EEL spectra will be considered here.

3.1. Maximum-intensity method

The most primitive way to retrieve information about WL intensities is to read the peak intensities from the edge spectra (Fig. 1). However, this results only in a rough estimate, because the continuum contribution is ignored. Nevertheless, if the spectra are recorded under the same experimental conditions (i.e., specimen thickness, composition, energy resolution, dispersion) one recognizes characteristic, Mn valency-dependent changes in the ratio of the maximum intensities, $I(L_3)_{max}/I(L_2)_{max}$, as we will show in Section 5.

3.2. Pearson method

In the WL extraction method of Pearson et al. [23] the continuum of the experimental edge region is approximated by a sum of two step functions in the case of 3d metals. For the Mn–L edge, those functions are separated by the energy difference between Mn–L_3 and Mn–L_2. First, a straight line is fitted to the spectrum in an interval beyond L_2 which is a few tens of eV wide. After extrapolating this line into the threshold region two steps are inserted, either

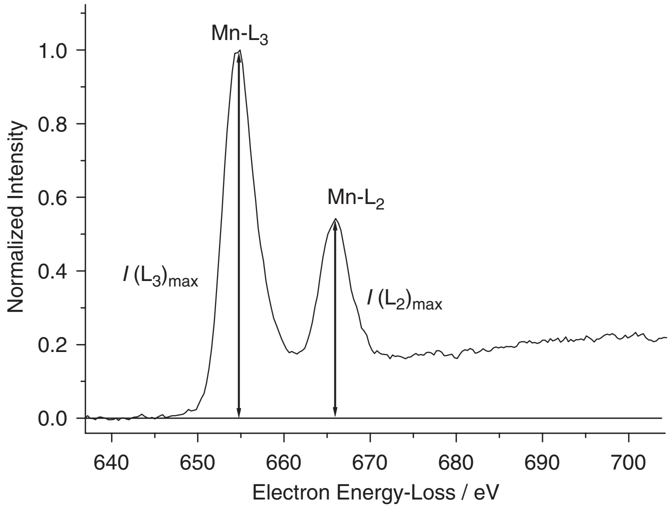

Fig. 1. Determination of maximum WL intensities of Mn_2O_3.