

Measuring valence information from chemical shifts in EELS on transition metal (Mn, Fe) oxides

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EELS spectra can be used to determine the valence of ionic materials in several ways^{1,2}. It is well known that especially the white lines in the 3d transition metals are sensitive to valence changes. Their positions, total intensity or L_3/L_2 ratio can be used to extract the valence information by comparing to reference spectra^{1,3}. One method which was shown to give superior results is to measure the distance in energy onset between the oxygen K edge and the transition metal L_{23} edge of oxides as was shown for niobium oxides by Bach et al.⁴. We adopt this method here and calibrated the measured energy distances between the oxygen K edge and the manganese or iron L_{23} edge against the transition metal valence for different reference compounds and applied this technique to measure the Mn valence in some new manganites.

Spectra of stable reference compounds of MnO [Mn^{2+}], Mn_2O_3 [Mn^{3+}], MnOOH [Mn^{3+}], MnO_2 [Mn^{4+}] and $CaMnO_3$ [Mn^{4+}] were acquired to study the relation between chemical shift and valence state. EELS data were acquired using a Gatan GIF200 system on a Philips CM30 microscope with an energy resolution of 0.8eV. All spectra were recorded in diffraction mode with a collection angle of 4.01 mrad and a convergence angle of 1.0 mrad. The obtained ELNES fine structure for the reference materials are in close agreement with published data for manganese oxides^{1,3,5}. For each material, spectra were recorded from 4 different regions to study inhomogeneity in the sample or thickness effects on the final result. The noise behavior of the method is studied by recording 100 spectra for each region. This allows also to check for time dependent changes in the sample due to beam damage. EELSMODEL^{6,7} was used to extract the ELNES fine structure of the recorded spectra. Multiple scattering was taken into account by convoluting a model of the spectrum with a recorded low loss spectrum as explained in detail in reference⁷. A power law background was used together with Hartree Slater cross sections for the Oxygen K and Manganese L_{23} edge.

The energy of the edge onset for both oxygen K and manganese/iron L_{23} edges is obtained by applying a threshold of 15% of the atomic cross sections in the continuum tail of the edge. The obtained onset difference is plotted together with error bars obtained from different regions (Figure 1). This spatial deviation is slightly larger than the noise from the 100 measurements in one region. Linear fitting shows a relation between this energy difference (ΔE) and the manganese valence (V_{Mn}) of :

$$\Delta E = a + b \cdot V_{Mn}$$

with $a = 103.026 \pm 0.364$ and $b = 2.527 \pm 0.103$, and R factor = 0.992. Using this relation, a new $Pb_4Mn_9O_{20}$ manganite was analysed. The determined Mn valence was found to be in excellent agreement with the results of chemical analysis and structure refinement.

The same method was applied to iron. The chosen iron reference compounds are $FeTiO_3[Fe^{2+}]$, $Fe_2O_3[Fe^{3+}]$, $Fe_2TiO_5[Fe^{3+}]$ and $BaFeO_3[Fe^{4+}]$. A linear relation between energy difference (ΔE) and Fe valence (V_{Fe}) was found:

$$\Delta E = a + b \cdot V_{Fe}$$

with $a = 174.147 \pm 0.127$ and $b = 1.794 \pm 0.050$, and R factor = 0.997. Both relations between energy difference and valence of Mn and Fe show the same tendency. They can be well fitted

by a linear relation. It is important to note that for different compounds with the same nominal valence, very similar onset energies have been found, indicating that the method is insensitive to the crystal structure. Comparing different regions for each compound also revealed that the method is insensitive to thickness and orientation changes.

The main advantages of this method over the more conventional methods like L_2/L_3 ratios are the independence of thickness, multiple scattering, energy resolution, acceleration voltage and energy drift. This indicates that the linear relationships could be generally applicable which removes the need for doing reference experiments for every microscope setup as long as the energy dispersion of the spectrometer is well calibrated. Apart from these advantages we have shown that the noise behavior of the method is very good. The procedure can be automated and will be implemented in EELSMODEL⁸.

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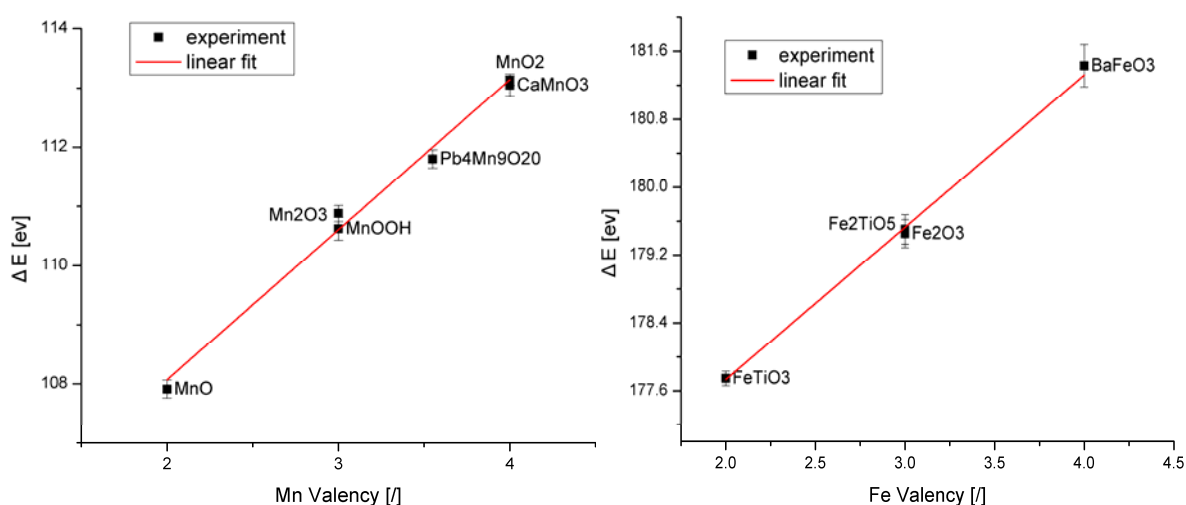


Figure 1. Experimental results of the energy onset difference between the O K-edge and Mn or Fe L_{23} -edge in various reference compounds. The red lines are the linear fittings. The Mn valence state of $Pb_4Mn_9O_{20}$ is measured to be $+3.47 \pm 0.07$ from this calibration (nominal +3.55).