Pushing EELS to the limits; Probing bonding and electronic structure at atomic resolution in low dimensional oxide structures

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Keywords: STEM-EELS, ELNES, Valency, Oxygen coordination

In (complex) metal oxides, bonding and electronic structure of the metal cations (in general oxygen coordination and valency) are of fundamental importance for the structural, electronic, magnetic, catalytic and ionic transport properties of the material. Even though the oxygen coordination and valency of metal cations in complex oxides can be determined by bulk methods like Mössbauer spectroscopy and in some conditions by diffraction techniques, local structural or changes in coordination/valency can be the key factors in many materials applications. For example, cation valency changes at the final terminating surface planes can be of vital importance for many catalytic processes, while changes in cation coordination or valency at defects like twin boundaries, grain boundaries and interfaces can greatly affect the electronic, optical and transport properties of bulk materials and thin films [1]. Being able to measure changes in valency and oxygen coordination at atomic resolution is therefore of extreme importance in many oxide materials, whether in the form of bulk material, thin films, nanowires or particles.

Atomic resolution elemental mapping has become feasible over the past years by means of spatially resolved electron energy-loss spectroscopy (EELS) and energy dispersive X-ray spectroscopy in a scanning transmission electron microscope (STEM-EELS and STEM-EDX). However, combining the atomic resolution capabilities of a STEM with the exquisite spectroscopic sensitivity to e.g. bonding and valency information from EELS fine structure long remained but an interesting prospect. The main issues hindering atomic resolution EELS fine structure investigation are poor EELS signal-to-noise ratios in experiments due to the need for simultaneous high spatial and energy resolution of the instrument. In the case of coordination mapping this problem is exacerbated further as, in general, changes in the fine structure of e.g. the $L_{2,3}$ edge of transition metals due to bonding or coordination changes are far more subtle than changes related to valency. Studies where bonding and coordination have been mapped at atomic resolution therefore long remained rare. Recent improvements in microscope instrumentation like high-brightness electron sources, aberration correctors and state-of-the-art spectrometers allow these issues to be overcome and atomic resolution fine structure investigation to be performed. Through use of a monochromator, spectroscopy with energy resolutions as low as 150 meV can be performed at atomic resolution and intricate details in the fine structure, linked to e.g. the coordination or valency of transition metals cations, can be investigated.

In this work, recent results on atomic resolution valency and oxygen coordination determination through investigation of the energy-loss near-edge structure (ELNES) in metal oxides will be presented. Two proof-of-principle experiments, the first demonstrating Fe and Co oxygen coordination mapping in bulk Ca_2FeCoO_5 (Figure 1), the second demonstrating Mn valency mapping in bulk Mn_3O_4 at atomic resolution show an excellent correlation between the transition metal ELNES and the valency/coordination of cations in metal oxides, even at atomic resolution. After demonstration of the principle, further examples of the application of the atomic resolution ELNES analysis to nanoparticle surfaces (surface reduction in CeO_{2-x} nanoparticles, Figure 2) and thin films (surface reduction in Fe_2O_x thin films) will be presented. Finally, potential pitfalls and current limits of the technique will be discussed [5].

References

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[5] S Turner gratefully acknowledges the Fund for Scientific Research Flanders (FWO). This work was supported by funding from the European Research Council under the 7th Framework Program (FP7), ERC grant N°246791 - COUNTATOMS and ERC Starting Grant 278510 - VORTEX.

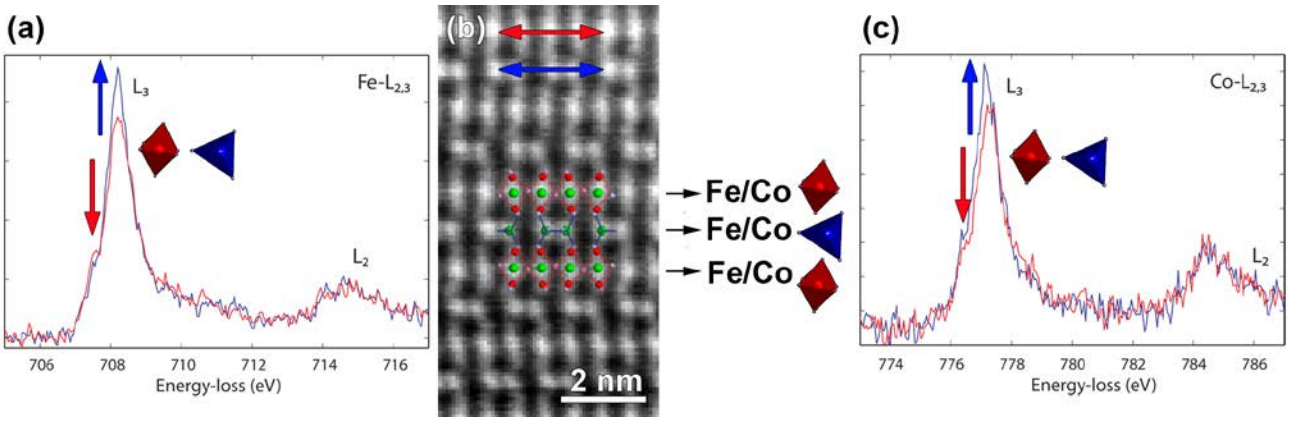

Figure 1. *Atomic resolution oxygen coordination mapping in Ca_2FeCoO_5 brownmillerite. The structure consists of layers of Fe and Co in alternating octahedral and tetrahedral coordination sandwiched in between layers of CaO. (a) Fe-$L_{2,3}$ edge summed over the first octahedral (red) and tetrahedral (blue) layer (b) Survey image indicating the area used for octahedral (red) and tetrahedral (blue) data summation (3 pixel width). (c) Co-$L_{2,3}$ edge summed over the first octahedral (red) and tetrahedral layer (blue). The EELS fine structure of the Co $L_{2,3}$ and Fe $L_{2,3}$ edges show specific features that are attributable to octahedral and tetrahedral coordination respectively.*

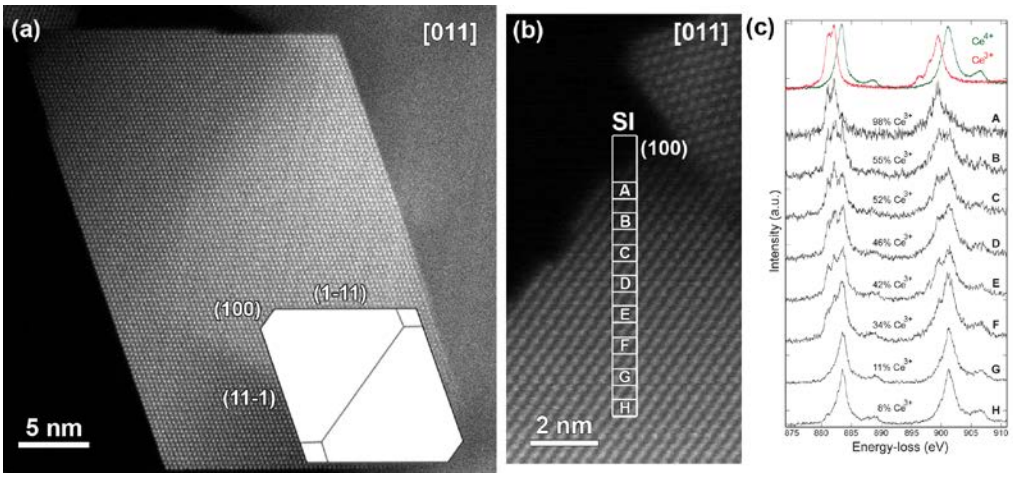

Figure 2. *Surface reduction in CeO_{2-x} nanoparticles. (a) HAADF-STEM image of a CeO_{2-x} nanoparticle along the [011] zone axis orientation with inset model. (b&c) Atomic resolution EELS scan over a (100) surface truncation: a clear reduction from Ce^{4+} to Ce^{3+} is measured at the atomic planes close to the surface of the nanoparticle through the fine structure of the Ce $M_{4,5}$ edge.*