Atomic Resolution Coordination Mapping in Ca$_2$FeCoO$_5$
Brownmillerite by Spatially Resolved Electron Energy-Loss Spectroscopy

Stuart Turner,* Johan Verbeeck,† Farshid Ramezanipour,§⊥ John E. Greedan,§⊥
Gustaaf Van Tendeloo,** and Gianluigi A. Botton†⊥∥

ABSTRACT: Using a combination of high-angle annular dark field scanning transmission electron microscopy and atomically resolved electron energy-loss spectroscopy at high energy resolution in an aberration-corrected electron microscope, we demonstrate the capability of coordination mapping in complex oxides. Brownmillerite compound Ca$_2$FeCoO$_5$, consisting of repetitive octahedral and tetrahedral coordination layers with Fe and Co in a fixed 3+ valency, is selected to demonstrate the principle of atomic resolution coordination mapping. Analysis of the Co-L$_{2,3}$ and the Fe-L$_{2,3}$ edges shows small variations in the fine structure that can be specifically attributed to Co/Fe in tetrahedral or in octahedral coordination. Using internal reference spectra, we show that the coordination of the Fe and Co atoms in the compound can be mapped at atomic resolution.

KEYWORDS: oxygen coordination, valency, electron energy-loss spectroscopy, EELS, energy-loss near edge structure, ELNES, Fe-L$_{2,3}$ edge, Co-L$_{2,3}$ edge, brownmillerite

INTRODUCTION

In complex transition metal oxides, the coordination and oxidation state of the transition metals is of fundamental importance. Both are known to be related to the structural, electronic, magnetic, catalytic, and ionic transport properties of (complex) oxides. The coordination and valency of transition metals in complex oxides can be determined by bulk methods like Mössbauer spectroscopy and in some conditions by diffraction techniques. However, local changes in coordination can be the key factors in materials applications. For example, coordination changes at surfaces are of vital importance for many catalytic processes while changes at defects like twin boundaries, grain boundaries, and interfaces can greatly affect the electronic, optical, and transport properties of bulk materials and thin films. The spatial resolution needed for the determination of coordination for these important problems is however not offered by classical bulk techniques like Mössbauer or diffraction methods.

Atomic resolution elemental mapping has become feasible over the past years by means of spatially resolved electron energy-loss spectroscopy (EELS) and, more recently, energy dispersive X-ray spectroscopy in a scanning transmission electron microscope (STEM-EELS and STEM-EDX) and has been used for local structure refinement. Even though STEM-EDX appears to allow more straightforward data acquisition and interpretation as compared to EELS, fine structure information like bonding or coordination cannot be obtained from X-ray spectra in the electron microscope with current spectrometers. Combining the atomic resolution capabilities of a STEM with the exquisite spectroscopic sensitivity to bonding and valence information from EELS fine structure is therefore a highly attractive prospect that would draw significant attention in the field of solid state chemistry, physics, and materials science. For transition metals, the shape of the L$_{2,3}$ edges, chemical shifts, and the L$_3$/L$_2$ ratio have all been used as a sensitive fingerprint for valence. A large correlation between the energy-loss near-edge structure (ELNES) and valence in transition metal oxides has been confirmed, even at atomic resolution, by experiments in literature. Using this correlation between ELNES and valency, oxidation state mapping at atomic resolution in CeO$_2$ nanoparticles and bulk Mn$_3$O$_4$ was recently demonstrated in some of our work. The main issues hindering atomic resolution valency and bonding measurements remain poor EELS signal-to-noise ratios because of the need for simultaneous high spatial and energy resolution of the instrument. This problem is exacerbated further as, in general, changes in the fine structure of the L$_{2,3}$ edge of transition metals because of bonding or coordination are far more subtle than changes related to valency. Studies where bonding and coordination have been mapped at atomic resolution are therefore rare, and usually the change in bonding...
coincides with a change in valency which also affects the EELS fine structure.\textsuperscript{8,21−23}

In this work, we set out to map the coordination of Fe and Co in a Ca\textsubscript{2}FeCoO\textsubscript{5} brownmillerite sample with constant Fe and Co valency but varying coordination.\textsuperscript{24} Ca\textsubscript{2}FeCoO\textsubscript{5} is a brownmillerite compound with an orthorhombic crystal structure (\textit{Pbnm}) with lattice parameters \textit{a} = 5.3652(3) Å, \textit{b} = 11.0995(5) Å, \textit{c} = 14.7982(7) Å, and is structurally similar to the well-documented Ca\textsubscript{2}Fe\textsubscript{2}O\textsubscript{5}.\textsuperscript{25} However, in Ca\textsubscript{2}FeCoO\textsubscript{5}, one unit cell axis is doubled compared to Ca\textsubscript{2}Fe\textsubscript{2}O\textsubscript{5} and other regular brownmillerites. Also, unlike typical brownmillerites, Ca\textsubscript{2}FeCoO\textsubscript{5} has two octahedral and two tetrahedral sites that are all crystallographically distinct, making the structure even more complex. The Fe and Co cations are stacked along the \textit{c}-direction in alternating octahedral and tetrahedral stacking layers in a constant 3+ valency (confirmed by our EELS data). The fact that Ca\textsubscript{2}FeCoO\textsubscript{5} is a mixed coordination/single-valency compound makes it an ideal candidate to demonstrate pure coordination mapping at atomic resolution; EELS fine structure variations over the tetrahedral and octahedral layers can unequivocally be assigned to coordination changes, and not valency variation. The presence of two different cation species (Fe, Co) in the sample can provide insight into the effect of coordination on the L\textsubscript{2,3} edge ELNES of both Co and Fe at atomic resolution.

\textbf{EXPERIMENTAL SECTION}

\textit{For experimental investigation}, samples were crushed and deposited dry onto a lacey carbon grid. The samples were investigated at the Canadian Centre for Electron Microscopy (McMaster University, Canada) using a FEI Titan "cubed" microscope equipped with a probe corrector, operated at 200 kV for Figures 1, 3, 4, and 5 and a similar instrument at the EMAT laboratory (University of Antwerp, Belgium) operated at its optimal acceleration voltage of 120 kV, for the data in Figure 2. For the data in Figures 1, 3, 4, and 5 the microscope was operated in STEM mode using a convergence semiangle \(\alpha\) of 18.5 mrad, yielding a probe size of \(\sim 1.0\) Å. The ADF inner collection semiangle was 60 mrad for imaging, and the spectrometer acceptance semiangle \(\beta\) was 70 mrad. The beam current was kept close to 40 pA for imaging and between 80 and 140 pA for spectroscopy. Suitable acquisition times (in the range of 10 ms/pixel to 20 ms/pixel) were chosen to avoid beam damage and provide the best combination of signal-to-noise ratio, spatial and energy resolution. Where needed, the monochromator was excited to provide an energy resolution of 250 meV.

The elemental maps in Figure 3 were generated in the case of Ca and O by mapping the intensity under the background subtracted edges. For Fe and Co, to improve the S/N ratio, the maps were generated through the so-called jump-ratio method. A post edge image was divided by a pre-edge image, yielding a qualitative result.\textsuperscript{13} When filtered, a 7\texttimes{}7 light low-pass filter was used in the Digital Micrograph software package. The data in Figure 5 was fitted to an octahedral and a tetrahedral internal reference component, being the summed fine structure spectrum of the top octahedral and the tetrahedral layer (which corresponds well to literature fine structure for 4 and 6 coordinated cations) using the EELS model software according to a method described in previous publications.\textsuperscript{18,19}

For the data in Figure 2 the microscope was operated in diffraction mode with excited monochromator providing an energy resolution of 250 meV. The convergence semiangle \(\alpha\) was \(\sim 1\) mrad, and the acceptance semiangle \(\beta\) was \(\sim 2\) mrad.

Image simulations were performed with the STEMSIM software package, a MATLAB based image simulation program capable of handling the complex interplay between elastic and inelastic scattering in the double channeling approximation. Elastic scattering was simulated with a Bloch wave approach (max wavevector 2.5 Å\textsuperscript{−1}), in 10 thickness steps to a total thickness of 20 nm using a unit cell sampling: 72\texttimes{}116 pixels per unit cell and a supercell of 3\texttimes{}1 unit cells. Source size broadening was taken into account using a Gaussian with 0.7 Å full width at half maximum. Proper agreement between simulations and experiments was only obtained using a random distribution of Fe and Co over the octahedral and tetrahedral sites, as discussed below. Inelastic scattering

\begin{figure}[h]
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\includegraphics[width=\textwidth]{figure1.png}
\caption{HAADF-STEM images of Ca\textsubscript{2}FeCoO\textsubscript{5} along the [100] (a) and [010] (b) zone axes orientation. The images show the repetition of octahedral and tetrahedral layers along the \textit{c} direction. An HAADF-STEM image simulation is inserted to the [100] zone axis image. Projected structural models for the [100] and [010] zone axis orientations are displayed in (c) and (d) respectively (Red = Co, Green = Fe, Brown = Ca, Pink = O). The unit cell is indicated by the black rectangles.
}
\end{figure}

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure2.png}
\caption{High resolution EELS data of Ca\textsubscript{2}FeCoO\textsubscript{5}. (a) EELS spectrum of Ca\textsubscript{2}FeCoO\textsubscript{5} showing the Ca-L\textsubscript{2,3} edge at 352 eV, the O-K edge at 529 eV, the Fe-L\textsubscript{2,3} edge at 708 eV, and the Co-L\textsubscript{2,3} edge at 779 eV simultaneously; (b) the Fe-L\textsubscript{2,3} edge in high resolution showing a shoulder to the L\textsubscript{3} edge at 709 eV, typical for Fe in a brownmillerite-type structure; (c) the Co-L\textsubscript{2,3} edge showing a far less-pronounced shoulder to the L\textsubscript{3} edge, and a small postpeak shoulder at \(\sim 782\) eV.
}
\end{figure}
was simulated using a relativistically corrected Dipole approximation with a hard Bethe ridge cutoff.

■ RESULTS AND DISCUSSION

Figure 1 shows two high-angle annular dark field (HAADF) STEM images of the Ca$_2$FeCoO$_5$ sample along the [100] and the [010] zone axis orientation. In both images, the c-axis is vertical, as indicated by the arrow in Figure 1b. The repetition of octahedral (example indicated by the red arrow) and tetrahedral (example indicated by the blue arrow) Co/Fe layers is apparent from the different structure of the layers in the [100] zone axis orientation and the contrast changes in the [010] zone axis orientation. Projected structural models for the [100] and [010] zone axis orientations are displayed in (c) and (d) respectively and correspond well to the HAADF-STEM images. A Bloch wave HAADF image simulation for a 20 nm thick crystal is inserted into Figure 1a, and agrees remarkably well with the experimental image.

Bulk Ca$_2$FeCoO$_5$ EELS data recorded over areas of several hundred nm are plotted in Figure 2. The spectrum in Figure 2a shows the Ca-L$_{2,3}$, the O-K, the Fe-L$_{2,3}$, and the Co-L$_{2,3}$ edge simultaneously. The Fe-L$_{2,3}$ and Co-L$_{2,3}$ are plotted in more detail (at a lower energy dispersion) in Figure 2b and 2c. To acquire these data, a monochromator was used to provide an energy resolution of approximately 250 meV. At a first glance, the fine structure of the Fe-L$_{2,3}$ and Co-L$_{2,3}$ edges is similar. This is to be expected, as both transition metals occupy similar positions within the Ca$_2$FeCoO$_5$ structure. Comparing the

Figure 3. Atomic resolution elemental maps for Ca, O, Fe, and Co along the [100] zone axis. (a) Raw Data. (b) Smoothed data. (c) Double channelling, inelastic Bloch wave image simulations for Ca, O, Fe and Co. The maps clearly show that Co and Fe are intermixed in each Co/Fe column, and demonstrate the repetition of the octahedral and tetrahedral coordination layers. (d) Averaged EELS spectra over the entire region showing the Fe/Co fine structure in the octahedral and tetrahedral layers at an energy resolution of ~1 eV.
Fe-L$_{2,3}$ edge to reference spectra in the literature reveals that the fine structure is identical to the literature fine structure for Fe$^{3+}$ in Ca$_2$Fe$_2$O$_5$. Moreover, literature data for Fe$^{3+}$ in octahedral and in tetrahedral coordination show that the shoulder of the L$_3$ edge at $\sim$709 eV can be used as a marker for the coordination of Fe; in compounds with octahedral Fe$^{3+}$, the shoulder is well-pronounced because of a t$_{2g}$-e$_g$ splitting of the L$_3$ peak. In compounds with solely tetrahedral Fe$^{3+}$, this shoulder is hardly visible. In Ca$_2$Fe$_2$O$_5$, the shoulder is less pronounced as Fe is present in both an octahedral and a tetrahedral coordination. A similar shoulder is visible near the Co-L$_3$ onset around 779 eV, although it is much less prominent than for the Fe-L$_3$ edge. This is in accordance with calculations and experiments in literature showing that both octahedral and tetrahedral Co$^{3+}$ (especially in the expected high spin state of Co$^{3+}$ in this compound) only display a small L$_3$ prepeak.

To acquire the spectroscopic data needed for coordination mapping, the so-called spectrum imaging technique was adopted. In this technique, the electron probe (in our setups the probe has a diameter of $\sim$1.0 Å) is scanned over the sample and an EELS spectrum is acquired in each point together with an annular dark-field signal as image reference. A first set of atomic resolution elemental maps, acquired at an energy resolution of $\sim$1 eV with the sample oriented along the [100] zone axis, is displayed in Figure 3. Elemental maps for Ca, O, Fe, and Co (top) are displayed together with low-pass filtered data (middle) and image simulations (bottom). Although some instabilities are present because of sample charging, the maps clearly show an unexpected intermixing of Fe and Co at both the octahedral and the tetrahedral sites, which are sandwiched in between layers of CaO. Indeed, a proper agreement between simulations and experiments could only be obtained using a random distribution of Fe and Co over the octahedral and tetrahedral sites. This appears to be at least in partial disagreement with a previously published neutron diffraction study where site ordering was found for Fe/Co on the tetrahedral sites, and warrants further investigation in the future. The contrast in the oxygen map is influenced by the presence of the nearby “heavy” Fe and Co columns, which commonly occurs for atomic resolution oxygen maps and is reproduced well in the simulation.

Figure 4 shows atomic resolution data acquired with an excited monochromator, providing an energy resolution of 250 meV. The overview image (Figure 4b), taken simultaneously with the EELS data, shows that working with an excited monochromator leads to only a limited loss in spatial resolution.
In Figure 4a and 4c data from a single layer of Co/Fe in octahedral and tetrahedral coordination (both indicated by arrows in the overview image, data averaged over 3 vertical pixels) is displayed. Contrary to the data at 1 eV energy resolution, clear differences in the Fe-L_{2,3} and the Co-L_{2,3} fine structure can be resolved by simple inspection. In the octahedral layer (red) the shoulder to the L_{3} edge for Fe, and to a lesser extent also for Co, is present in good agreement with the data from literature.\(^{20}\) In the case of octahedral Co, a small shoulder is also present behind the L_{3} maximum (at \(\sim 782\) eV), in agreement with literature.\(^{27}\) The data acquired from a single tetrahedral layer on the other hand (blue) shows a far less distinct shoulder in the case of Fe. Concomitant with this change, the L_{3} signature for Fe and Co-L_{3} in the tetrahedral coordination peaks higher and slightly narrower than the L_{3} for the octahedral sites (after alignment of the data to the integral under the L_{3,1} edge). This is at least in part because of the white line ratio; as the L_{3}/L_{2} white lines is known to remain constant for constant valency, the intensity “lost” under the L_{3} shoulder is compensated by a higher and narrower L_{3} peak. For tetrahedral Co, the small shoulder at 782 eV is also subdued.\(^{26}\) In all, clear exquisite differences in fine structure are visible between the octahedral and the tetrahedral spectra for both Fe and Co at constant valence. These differences can be used to map the coordination of the Fe and Co cations in the structure using the averaged EELS signals from Figure 4a and 4c as internal references.

In Figure 5, the internal reference data for Fe and Co in the two distinct coordinations are fitted to the entire acquired EELS database, following the procedure from earlier work on atomic resolution valency mapping.\(^{18,19,30,31}\) Fitting the internal “octahedral” and “tetrahedral” reference data to each acquired spectrum allows coordination maps with the weight of each component to be generated. Prior to fitting, the data cube was rebinned in X and Y direction by a factor of 2 to improve the S/N ratio in the individual spectra. The results of the fit are displayed in Figure 5b,c. The octahedral and tetrahedral component maps of the transition metals clearly follow the atomic contrast of the separate coordination layers in the ADF survey image. Moreover, each component map peaks at the correct coordination layer. These results clearly demonstrate that coordination can be mapped in these structures down to atomic resolution. Because of the small variations in the fine structure of the Fe L_{2,3} and Co L_{2,3} edges used for mapping, lateral resolution is not clearly obtained.

The results obtained in Figures 3 and 5 clearly indicate that using the fine structure of EELS data acquired at atomic resolution with a high energy resolution, advanced electron microscopy can surpass elemental mapping, and provide atomic resolution information on, for example, oxygen coordination. The data presented in this paper also suggests that mapping of valence and coordination independently, along with the elemental map, can be done in the future. As well, this study shows that Fe^{3+} and Co^{3+} are distributed in a roughly random manner over both sets of the octahedral and tetrahedral sites in Ca_{2}FeCoO_{5}. This is at least in partial disagreement with the results of a published refinement of neutron diffraction data where Fe/Co site order was found on the tetrahedral sites. The origin of this discrepancy is unclear at the moment, but it might be related to the inherent difference between the two methods: neutron diffraction being a bulk probe as opposed to the electron microscopy which is a local method. A new neutron data set has been obtained and refinements are underway to reconcile this discrepancy.

**CONCLUSION**

We have demonstrated the possibility of coordination mapping by atomically resolved high resolution EELS in an aberration-corrected electron microscope, through the example of single valency/mixed coordination cation compound Ca_{2}FeCoO_{5}. Detailed analysis of the fine structure of the Co-L_{2,3} and the Fe-L_{2,3} edges showed small variations in the fine structure that could be attributed to Co/Fe in tetrahedral or Co/Fe in octahedral coordination and that were in excellent agreement with literature spectra for octahedral and tetrahedral coordinated Fe^{3+}/Co^{3+}. Using the spectra from octahedral/tetrahedral Fe/Co layers as a internal reference (and in the future possibly theoretical spectra to identify unknown materials), the coordination of the Fe and Co atoms in the compound could be mapped at atomic resolution. These experiments open the gate for coordination determination at surfaces, defects, and grains boundaries in a plethora of complex oxide materials that have been out of reach in the past because of the lack of suitable analysis techniques for the study of valence and coordination as input for solving their structure.

**AUTHOR INFORMATION**

Corresponding Author

*E-mail: stuart.turner@ua.ac.be.

Notes

The authors declare no competing financial interest.

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