

Applications of High-Resolution EELS Near-Edge Structures in Complex Oxides

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Electron energy loss near edge structures obtained with high energy resolution can provide a wealth of information on fine features previously not detectable with conventional resolution energy loss spectroscopy [1-3]. These fine features can provide key information on structure and bonding in materials including information on valency, and spin state and coordination of transition metal atoms with high spatial resolution. When the technique is applied to complex crystalline structures, it is possible to probe effects of substitutions in the lattice and their influence on the electronic structure of materials. In our recent work we have therefore attempted to probe the systematic trends in a few series of compounds potentially attractive for their functional properties and their structure in order to provide useful information on their properties.

Experiments were carried out on a FEI Tecnai-200 FEG equipped with a monochromator yielding a resolution of about 0.1eV measured at the full width at half maximum of the zero-loss peak. Recent experiments have further demonstrated the effect of numerical deconvolution on low energy loss spectra obtained with a monochromator [4] these being particularly useful for the enhancement of features down to 0.5eV losses. A variety of samples in the perovskite based series $\text{Sr}_2\text{Ru}_{2-x}\text{Co}_x\text{O}_{6-8}$, the ilmenite series MTiO_3 where M is Mn, Co, Fe or Ni, as well as spinels in the MnCu_2O_4 series were studied in this work. Transmission electron microscopy samples were prepared by crushing powders and dispersing them on C coated Cu grids. Spectra were obtained with an energy resolution of 0.1-0.2eV throughout this work. Calculations of energy loss spectra to support our interpretation of structure and valency were carried out using the atomic multiplet technique described elsewhere [5].

As examples of the work, we show here spectra of the Mn L_{2-3} and Co L_{2-3} edges in the ordered corundum (ilmenite) structure MnTiO_3 and CoTiO_3 respectively where multiplet calculations indicate unambiguously the presence of high-spin Mn^{2+} and Co^{2+} in the octahedral sites (figure 1a, b) and the clear benefits of enhanced energy resolution of the spectra. In the series of ilmenite-based compounds, studies of the O K edges show the similarities of the spectra with TiO_2 polytypes structures thus indicating the strong and dominant hybridization of the Ti-3d band with the O-2p orbitals (Fig. 2) and the intrinsically broad near-threshold features [6]. The effect of the enhanced resolution is also demonstrated in the Co L_{2-3} edges in the series of $\text{Sr}_2\text{Ru}_{2-x}\text{Co}_x\text{O}_{6-8}$ compounds where it is possible to deduce, with atomic multiplet calculations, that the Co atoms are in a high-spin configuration and 3+ oxidation state (figure 3). With increasing Co content in the series ($x=0.5, 1.0$ and 1.5), the spectra show no significant changes in either the oxidation or spin state suggesting that the structural distortions detected by X-ray work, as the composition is altered, do not result in significant changes in the magnetic structure of Co. These results clarify some trends in magnetic measurements [7]. Further work on compounds based on spinel structure and oxides with highly correlated electrons will be presented [8].

References

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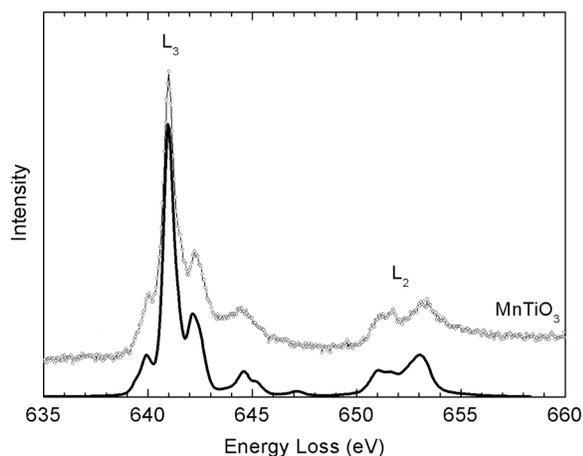


Figure 1a) Mn L_{2-3} edge in MnTiO_3 ; full line multiplet calculations for Mn^{2+} .

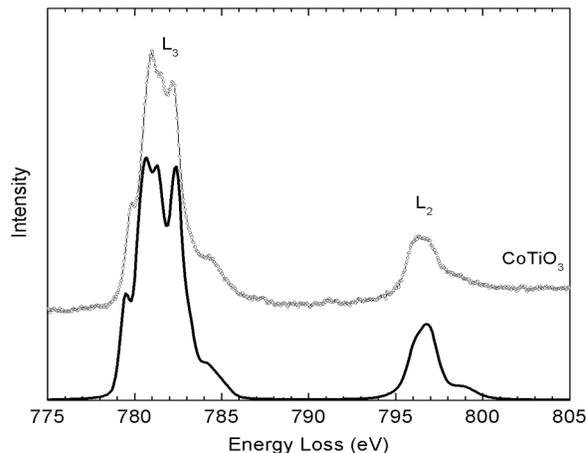


Figure 1b) Co L_{2-3} edge in CoTiO_3 full line multiplet calculations for Co^{2+} .

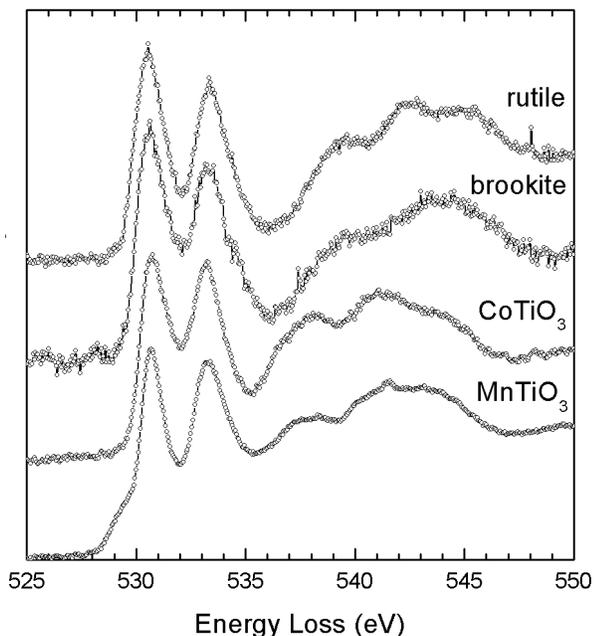


Figure 2) O K edges in MnTiO_3 , CoTiO_3 and TiO_2 (brookite and rutile).

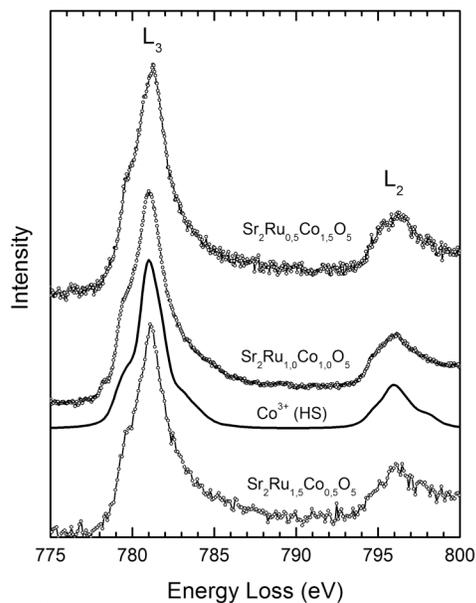


Figure 3) Co L_{2-3} edges in $\text{Sr}_2\text{Ru}_{2-x}\text{Co}_x\text{O}_{6-\delta}$, full line: multiplets for Co^{3+} high-spin state.