

Electron energy loss spectroscopy at high spatial resolution: from elemental to orbital mapping

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1. INTRODUCTION

Over the last decade, aberration correctors, monochromators, brighter electron sources and the improved stability of electron optics in the transmission electron microscope have drastically improved the capabilities of analytical electron microscopy. Atomic-scale structural and chemical analyses of a wide range of materials are now routinely available. In particular, electron energy loss spectroscopy (EELS) in the scanning transmission electron microscope (STEM) allows to combine both spatial and chemical information, via elemental mapping in crystals at the atomic level [1], by rastering a high current sub-Ångström probe over the region of interest of the specimen. Using STEM-EELS, elemental mapping can provide a direct and clear evidence of the atomic-scale structure of a material. In addition, core-loss EELS can directly probe the unoccupied density of states allowed by transition rules. The energy loss near edge structure (ELNES) contains relevant information on the electronic structure, chemical bonding, and thereby related properties of the material under investigation. It is of particular interest to obtain spatially-resolved information on the electronic structure by selecting specific spectral features of the ELNES. Indeed, these fine structures arise from transitions to unoccupied states of a particular energy, thereby allowing the identification of localized states at the atomic scale.

2. RESULTS

2.1 Experimental details

STEM-EELS experiments were performed on a FEI Titan 80-300 cubed, equipped with image and probe correctors, a monochromator, and operated at 80kV. Specimens were prepared by either wedge polishing or focus ion beam milling. Interpretation of the experimental data presented here are supported inelastic channelling calculations, where the elastic scattering is taken into account from a multislice approach, and inelastic scattering was modeled by diagonalizing the mixed dynamic form factor [2] obtained from first principle calculations (WIEN2k code) [3].

2.2 Results and discussion

The relevance of identifying spatially-resolved fine structures is shown in the case of cuprate superconductors. Indeed, the localization of holes/electrons in these compounds is of primary interest to further understand their physical properties. Although other unoccupied states spectroscopy such as x-ray absorption spectroscopy (XAS) provide valuable spectral information, performing EELS measurements within the TEM has the advantage of higher spatial resolution [4-6].

As an example, the chain-ladder superconductor $\text{Ca}_x\text{Sr}_{1-x}\text{Cu}_{24}\text{O}_{41}$, made of CuO_2 chains and Cu_2O_3 ladders, is investigated by STEM-EELS at the atomic level (see Figure 1a,b) [6]. The atomic resolution achieved by aberration-corrected STEM-EELS allows the study of the hole distribution atomic column by column, in contrast to XAS that integrates over all Cu-rich planes in the structure. Fine structures at the O-K and Cu-L_{2,3} edges are in good agreement with existing XAS results. Analysis of the hole distribution is performed from the O-K pre-edge ELNES, which is composed of the O-2p hole band, and the upper Hubbard band (see Figure 1c) [7]. Using the spectrum imaging technique available in STEM-EELS, it is demonstrated that the holes lie preferentially within the CuO_2 chains of the structure. The quantitative analysis of the hole concentration is compared with available results from existing data in the literature. Furthermore, the effect of electron channelling on the quantification is discussed based on simulations.

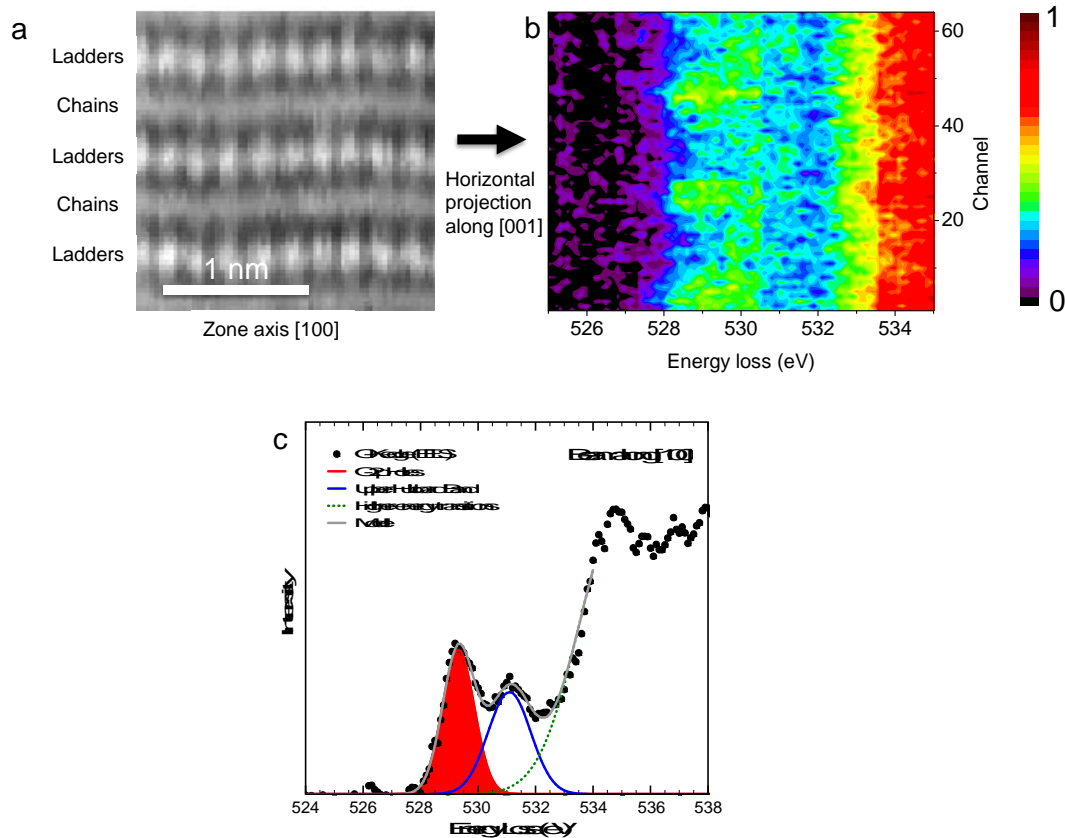


Figure 1. Spectrum image data set of $\text{Ca}_x\text{Sr}_{1-x}\text{Cu}_{24}\text{O}_{41}$ illustrating simultaneously acquired STEM-HAADF image (a) and O-K pre-edge EELS spectra projected along [001] (b). Variations in the intensity of the pre-edge fine structures are observed from chains to ladders. (c) Monochromated O-K edge of $\text{Ca}_x\text{Sr}_{1-x}\text{Cu}_{24}\text{O}_{41}$ recorded in [100] zone axis. The pre-edge fine structures are fitted with Gaussian functions.

Finally, real-space mapping of individual atomic orbitals in bulk specimens will be shown on rutile (TiO_2) single crystal [8]. Asymmetric features corresponding to the direction of the Ti-O bonds are highlighted in the experimental maps, and supported by calculations. Such direct visualization allows for the experimental verification of theoretical predictions of electronic states, and interestingly provides a way to directly investigate electronic states at interfaces or defects, where capabilities of numerical simulations remain limited.

3. CONCLUSION

Through different examples, this work highlights how the combination of ELNES analyses in aberration corrected STEM can be used at different scales, from elemental mapping to the identification of localized states at the atomic level, ultimately leading to a direct visualization of electronic orbitals. This approach provides new insights into a wide range of problems in materials science, such as improving the understanding of the electronic properties of cuprate superconductors, and also opens the way to probe and interpret electronic states at interfaces or defects. The results presented here also highlight some challenges in data interpretation, with the need to rely on extensive numerical simulations.

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