

## Probing Functional Oxides by Ultra-High Resolution EELS under Variable-Temperature Stimuli

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The quest for advanced functional materials towards higher performance remains a key area in which complex oxides are a promising class of materials across a large spectrum of functionalities. Transition-metal (TM) oxides exhibit a strong interplay between their charge, lattice, orbital, and spin degrees of freedom that are usually further activated under external stimuli. These phenomena originate from subtle but critical local modulations of their atomic and/or electronic structures that strongly govern their physical properties at the macroscopic scale. Hence the requirement to probe the nanostructure's local properties in their native environments using *in situ* ultra-high resolution electron spectromicroscopy.

The field of spectromicroscopy relies on a few available techniques capable of providing chemical state information, local bonding environments and electronic structures for the characterization of nanostructures, e.g. buried interfaces, anisotropic structures or individual ones. Electron Energy-Loss Spectroscopy (EELS) performed within a Scanning Transmission Electron Microscope (STEM) is one of the techniques of choice among other very powerful but mainly synchrotron-based techniques. Probing the chemical and electronic natures of atomic columns via spectroscopic signals has become routine with Cs-correctors since 15 years now. In stark contrast sub-10 meV electron monochromators (MC) emerged only very recently [1], and are game-changers for nanomaterials characterization. Indeed, such ultra-high spectral resolutions open the way for probing locally the phonon response [2], the band gaps and states of semiconductors, or the TM valence and spin states [3] with sub-nanometer spatial resolution.

Here we present very recent proof-of-principle STEM/EELS experiments performed on Cs-correctors STEM NION microscopes either at high-temperature on the UltraSTEM 200 using the Protochips heating MEMS system or at low-temperature using the monochromated instrument, i.e. CHROMATEM coupled with a HennyZ liquid nitrogen stage holder. Archetypal materials such as the  $\text{Co}_3\text{O}_4$  spinel structure and  $\text{V}_2\text{O}_3$  system were investigated first to evaluate how deep their electronic structures can be revealed at the local scale under tuneable temperature stimuli. Hence  $\text{Co}^{2+/3+}$  valence mapping were successfully achieved already at  $100^\circ\text{C}$  (Fig. 1) demonstrating the feasibility of studying charge-ordered oxide systems above room temperature. Besides new insights into  $\text{V}_2\text{O}_3$  systems were investigated by probing its temperature-driven metal-to-insulator transition (MIT) [4] down to the nm-scale through its core-loss fine structures' evolution upon low-temperature thermal cycling (Fig. 2). These experimental results are of main importance for improving MIT switching efficiency at the macroscopic scale and for a deeper understanding of the electronic states' mechanisms governing MIT. [5]

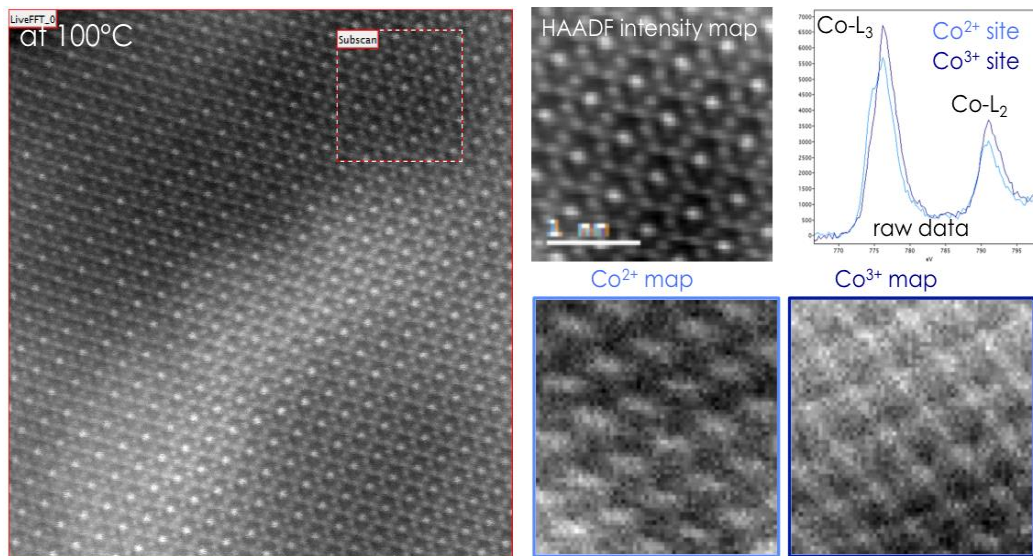
[1] OL Krivanek *et al*, Nature **514** (2014), 209.

[2] MJ Lagos *et al*, Nature **543** (2017), 529.

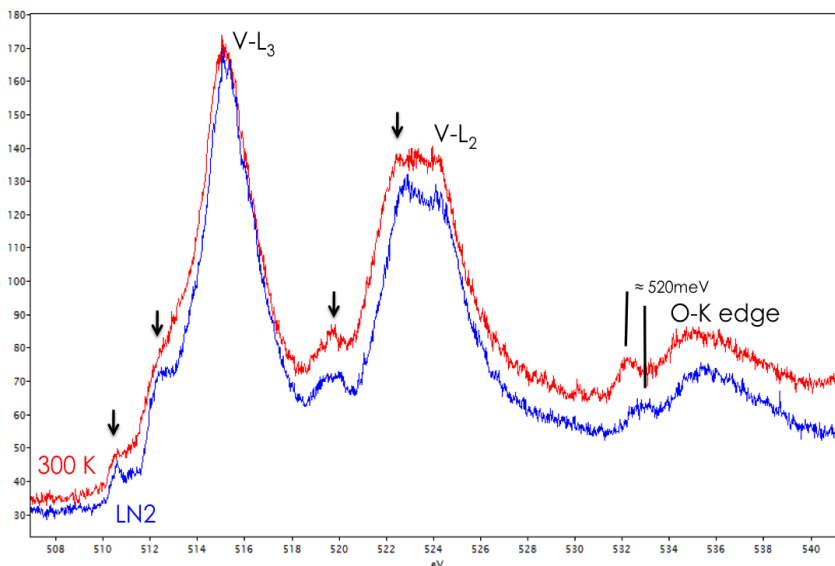
[3] F de Groot and A Kotani. “Core Level Spectroscopy of Solids” CRC Press.

[4] H Abe *et al*, Jpn J Appl Phys **38** (1999), 1403.

[5] This work has received support from the National Agency for Research under the program of future investment TEMPOS- CHROMATEM with the Reference No. ANR-10-EQPX- 50.



**Figure 1.** Valence state mapping acquired at 100°C in model  $\text{Co}_3\text{O}_4$  spinel oxides



**Figure 2.** Core-loss fine structures of  $\text{V}_2\text{O}_3$  thin films across the temperature-driven MIT