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Aberration corrected STEM-EELS study of the hole distribution in cuprate superconductors

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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 spectrometry (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, in a first approximation, core-loss EELS can directly probe the unoccupied density of states allowed by transition rules. The energy loss near edge structures (ELNES) contain relevant information on the electronic structure, chemical bonding, and thereby related properties of the material under investigation. It is of particular interest that spatially-resolved information on the electronic structure and properties can be obtained 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].

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 unarguable advantage of higher spatial resolution [3,4].

As an example, the chain-ladder superconductor $Ca_xSr_{1-x}Cu_{24}O_{41}$, made of CuO_2 chains and Cu_2O_3 ladders, is investigated by STEM-EELS at the atomic level (see Figure 1a,b). The STEM-EELS experiments were carried out in two aberration-corrected FEI Titan microscopes equipped with monochromators and high-resolution Gatan EELS spectrometers. The atomic resolution achieved by aberration-corrected STEM-EELS allows the study of the hole distribution atomic column by atomic column, in contrast to XAS that integrates over all Cu-rich planes in the structure. Fine structures at the O-K and $Cu\text{-}L_{2,3}$ 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-2*p* hole band, and the upper Hubbard band (see Figure 1c) [5,6]. Using the spectrum imaging technique available in STEM-EELS, we demonstrate that the holes lie preferentially within the CuO_2 chains of the structure. The quantitative analysis aspects of the hole concentration determination are discussed, in comparison with available results from existing data in the literature. Furthermore, the effect of channeling on the quantification is discussed based on simulations.

This work highlights the combination of ELNES analyses with atomic resolution in the aberration corrected STEM, to improve the understanding of the electronic properties of cuprate superconductors [7].

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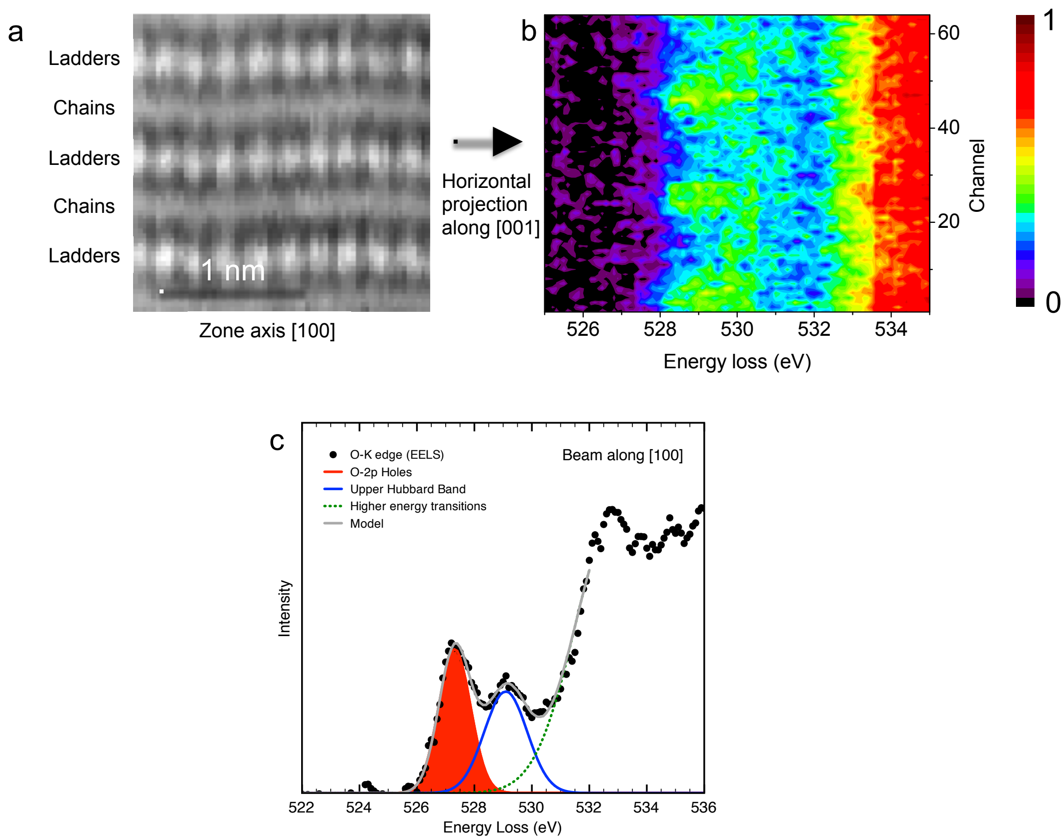

Figure 1. Spectrum image data set of $Ca_xSr_{1-x}Cu_{24}O_{41}$ illustrating simultaneously acquired STEM-HAADF image (a) and O-K pre-edge EELS spectra projected along [001] (b). Variations in the intensity of the pre-edge fine structures are observed from chains to ladders. (c) Monochromated O-K edge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