ATOMIC SCALE ANALYSIS OF COMPLEX OXIDE INTERFACES

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Aberration correction in the Scanning Transmission Electron Microcope (STEM) is pushing the achievable spatial resolution for imaging and spectroscopy into the sub-angstrom regime, providing a new level of insight into the structure/property relations of complex materials. The combination of atomic-resolution Z-contrast scanning transmission electron microscopy and electron energy loss spectroscopy (EELS) represents a powerful method to link the atomic and electronic structure of solids to macroscopic properties. Images now show greatly improved contrast and signal to noise ratio, sufficient to allow sensitivity down to the single atom level in both imaging and spectroscopy. Therefore, the electronic structure of solids can now be probed with a spatial resolution close to 1 Å[1,2], allowing the properties of interfaces to be probed in unprecedented detail.

This work presents several examples of atomically resolved studies of the relationship between structure and electronic properties of complex oxides and oxide interfaces. The first concerns the spectroscopic identification of single atoms in $CaTiO_3/La_{1-x}Ca_xTiO_3$ superlattices with low La doping, which has been investigated to determine the sensitivity to single La atoms [3]. These can be identified through intensity traces, allowing single atom EELS detection (Fig 1). Another example will address charge ordered stripes in manganites. In $Bi_{0.37}Ca_{0.63}MnO_3$ an atomically-resolved stripping of the Mn $L_{2,3}$ EEL spectra has been found, which demonstrates inequivalent Mn planes that correlate with two distinct formal oxidation states (Fig 2).

Also, the analysis of interfaces in superconducting/ferromagnetic $YBa_2Cu_3O_{7-x}/La_{0.67}Ca_{0.33}MnO_3$ (YBCO/LCMO) superlattices will be shown. A high resolution STEM image obtained with a high angle annular field detector is shown in figure 3. Such interfaces are coherent, and free of defects. By means of high spatial resolution EELS disorder parameters like chemical interdiffusion can be analyzed by studying how the intensity associated with the different edges changes across the interface. Figure 3(b) show how the intensity of the edges of La (open circles), Mn (solid circles) and Ba (solid squares) decays abruptly at the interface, so that chemical interdiffusion can be disregarded. From the point of view of the electronic properties, direct evidence of hole doping from the ferromagnetic layer into the superconducting layers will be shown, as depicted in figure 3(c), where the decay of the intensity of the pre peak feature in the O K edge as a function of the distance to the interface is shown. This feature is associated with density of holes in the YBCO layer [4]. This mechanism provides a simple explanation for the low values of the Tc in these superlattices.

References:

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Figures:

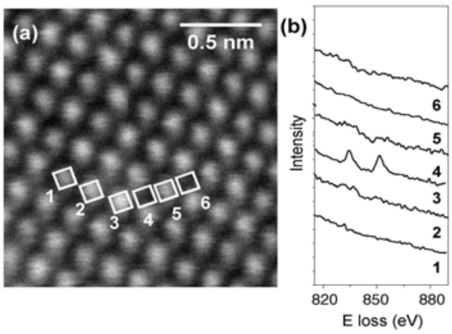

Figure 1: (a) Z-contrast image of a $La_{0.025}Ca_{0.9975}TiO_3$ layer in a $CaTiO_3/La_{1-x}Ca_xTiO_3$ superlattice, showing an isolated La ion (3). (b) EELS spectra acquired while placing the beam on the positions marked on figure 1(a).

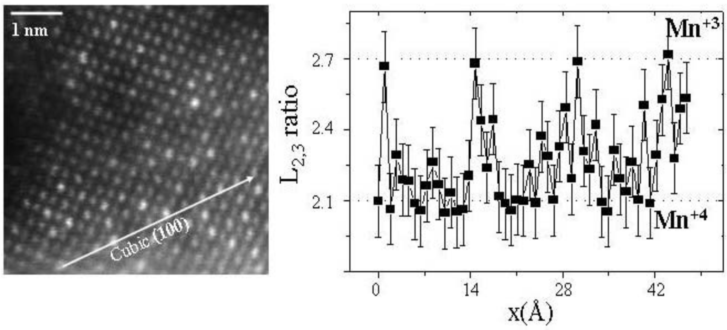

Figure 2: (a) Z-contrast image of a $Bi_{0.37}Ca_{0.63}MnO_3$ manganite. (b) Dependence of the $L_{2,3}$ ratio, the formal oxidation state of the Mn atoms, with position when scanning the beam along the arrow marked on figure 2(a). Dotted lines mark the expected $L_{2,3}$ ratio of Mn^{+3} (top) and Mn^{+4} (bottom).

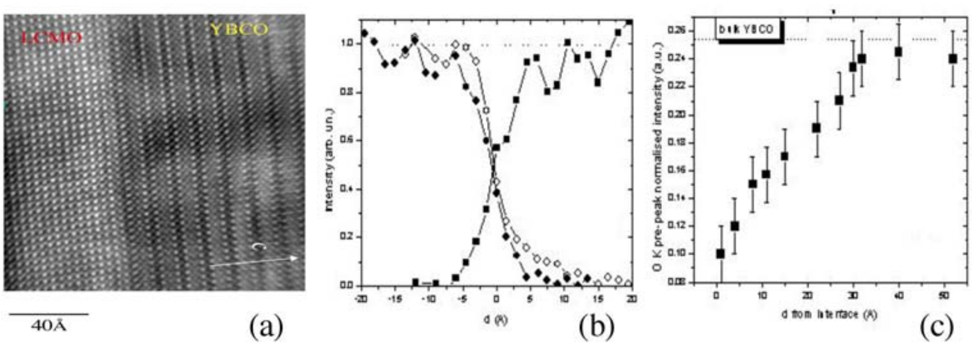

Figure 1: (a) Image of a LCMO/YBCO interface. (b) Intensity of the edges of La (open circles), Mn (solid circles) and Ba (solid squares) as a function of the distance to the interface. (c) Dependence of the density of holes in YBCO as a function of the distance to the interface.