Probing electron states at interfaces in perovskite oxides using the 3d transition metal L edges

J.-L. Maurice¹, D. Imhoff² and C. Colliex²

¹ Unité Mixte de Physique CNRS/Thales, UMR CNRS 137, Domaine de Corbeville, 91404 Orsay cedex, France
² Laboratoire de Physique des Solides, UMR CNRS 8502, Université Paris-Sud, 91405 Orsay cedex, France

The oxygen octahedral cage in perovskites is often occupied by a transition metal cation. The electron occupancy of the valence levels of that cation strongly depends on the electrostatic charge of its surroundings: charge of other cations and presence of oxygen vacancies. The band structure itself also depends on the distortions of the site (Jahn-Teller effect). The density of states available for excited electrons at such a site is thus particularly sensitive to the proximity of an interface. EELS L-edges of 3d transition metals correspond to excitations of electrons from the 2p core levels to a superposition of empty 4s and 3d levels. Their shapes can in some cases be analysed directly in terms of local composition and structure. The case of Ti in SrTiO₃ is quite exemplary in this respect as its valency being 4+, its 4s and 3d-bands are completely empty. Moreover, its valency can change to 3+ at interfaces or in the presence of oxygen vacancies, and Muller and co-workers have shown that such variations appear indeed very clearly in the EELS signal [1]. Here, we analyse the behaviour of the transition metals Mn and Ti L signals at the (001) interface between SrTiO₃ (STO) and La₂/₃Sr₁/₃MnO₃ (LSMO) [2]. The changes occurring at this interface, concern only the Mn ions in LSMO, while the edges remain unmodified for the Ti ions on STO’s side, and they can be correlated to variations in magnetic coordination. Preliminary measurements concerning Ti edges at the interface of STO with perovskites having cations of different valences, such as LaAlO₃ and La₀.₅Sr₀.₅TiO₃ [3], will also be reported.

Fig. Evolution of the Mn-L edge when the incident probe crosses the LSMO/STO interface with 0.3 nm steps. The signal is regularly decaying to zero in the centre of a 5 nm tunnel junction

References
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