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MS-14-O-1967 Probing the local electronic configurations in tubular cobaltites : impact of the Co^{2+}/Co^{3+} distribution on the transport and magnetic properties

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Among the numerous different oxide systems, the cobaltites present fascinating and complex physical properties directly correlated with their electronic structure. A strong interplay exists in these Co-based systems between (i) valence and spin states and (ii) low dimensionality and structural anisotropy, all of these yielding the emergence of unexpected magnetic and thermoelectric (TE) functionalities as illustrated in Na_xCoO_2 [1].

The misfit-layered cobalt oxides built from similar cobalt layers have triggered intensive works regarding their remarkable TE properties at high temperatures. A real driving force of this misfit family is the CoO_2 2D hexagonal layers turning out to be at the origin of its metallicity combined with a large thermopower, and more largely of interesting magnetic and electronic phenomena [2].

Another cobalt oxide, $Bi_4Sr_{12}Co_8O_{28-\delta}$, derived from the 2201-type cuprates reveal an original tubular structure. This complex structure with a 2D structure (24*24*5.4Å^3) can be viewed as a stacking of n=2 $[Bi_2Sr_2CoO_6]$ slices separated by single Co-deficient pervoskite $[Sr_8Co_6O_{16-\delta}]$ layers. Hence, squared pillars based on CoO_x polyhedra create tubular cavities at the crossing of two $[Sr_8Co_6O_{16-\delta}]$ layers. Besides the complexity of this anisotropic structure, the nature of the CoO_x pillars can be fine-tuned by adjusting the oxygen stoichiometry, therefore playing a key role on the local electronic configurations of these systems. As in misfit cobaltites, the Co-tubular family reveals peculiar transport properties and magnetic transitions while their local electronic configurations remain unresolved to date. In these bidimensional cobaltites, one of the pivotal questions is the key role played by each type of Co sites.

Here we attempt to shed light on the $[Bi_2Sr_2CoO_6]_2[Sr_8Co_6O_{16-\delta}]$ n=2 member by resolving its atomic structure (Fig. a)) using an aberration-corrected STEM – the NION UltraSTEM200 – coupled to EELS. Relying on high-energy resolution, we probe locally the Co-$L_{2,3}$ and O-K fine structures, which are highly sensitive to the mixed valence-states and the hybridization geometries. In particular, distinct spectroscopic signatures related to inequivalent oxygen sites are probed in the real-space as illustrated in Fig. b). Hence two different oxygen fine structures ($O_{(3)}$ and $O_{(4)}$) are identified on the Co sites illustrating the original local bonding environment in these Co-tubular oxides.

[1] I. Terasaki, Y. and K. Uchinokura, Phys. Rev. B 56, R12685 (1997)

[2] S. Hébert, W. Kobayashi, H. Muguerra, Y. Bréard, N. Raghavendra, F. Gascoin, E. Guilmeau, A. Maignan. Phys. Stat. Sol. A 210, 69-81 (2013)

[3] D. Pelloquin, A. C. Masset, A. Maignan, M. Hervieu, C. Michel, B. Raveau, J. Solid State Chem.148, 108-118 (1999)

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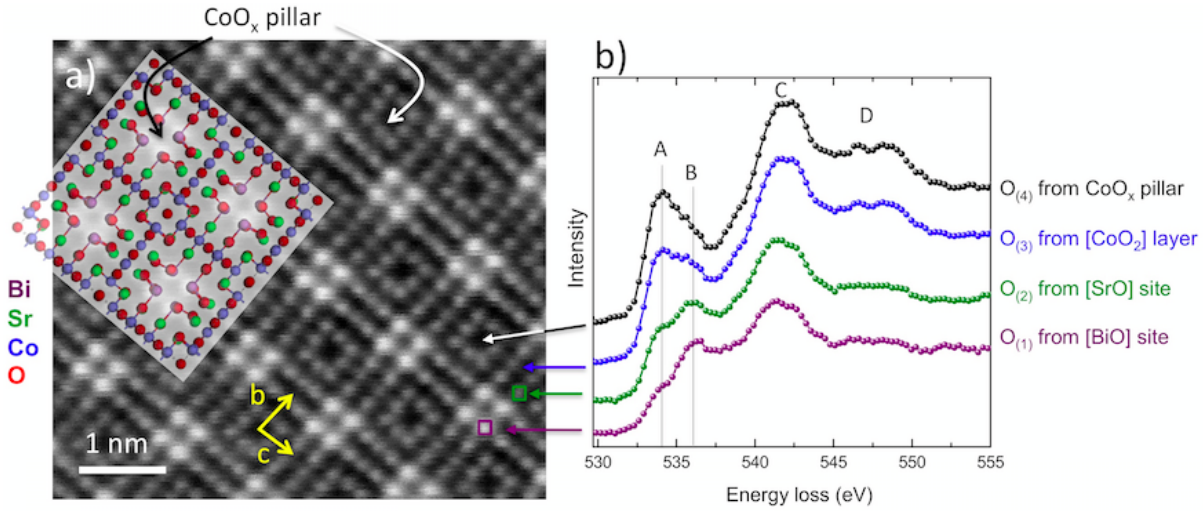

Fig. 1: a) STEM-HAADF image along the [100] direction and the corresponding structural model of the $[Bi_2Sr_2CoO_6]_2[Sr_8Co_6O_{16-\delta}]$ phase (inset). b) O-K edge fine structures extracted at four distinct oxygen sites. Each spectrum is integrated over 4 x 4 pixel with a 10ms/pixel acquisition time.