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Atomic scale studies of the electronic properties of CMR manganese oxides

M. Varela, * V. Peña, ** Z. Sefrioui, ** W. Tian, * A.R. Lupini,* D.G. Mandrus, * J. Santamaria,** S.J. Pennycook. *

* Condensed Matter Sciences Division, Oak Ridge National Laboratory, PO Box 2008, Oak Ridge, TN 37831
** GFMC, Dpt. Fisica Aplicada III. Universidad Complutense de Madrid. Madrid 28040, Spain.

The large number of potential applications of manganites exhibiting colossal magnetoresistance (CMR) has led to extensive experimental and theoretical investigations. However, the physical mechanisms underlying CMR remain elusive. One of the long-standing issues associated with these systems is the nature of the spatial modulation known as the charge ordered (CO) state. These are striped phases, insulating and often antiferromagnetic, which arise in the vicinity of metal insulator transitions occurring at half doping, and extend themselves into wide regions of phase diagrams. A deeper understanding of its nature will not only provide the key to harness the electronic properties of manganites, but also and to understand the nature of stripes in complex oxides.

In this work we report the first direct mapping of the electronic structure of the CO state in bulk $Bi_{0.37}Ca_{0.63}MnO_3$ (BCMO) samples at the atomic scale. Z-contrast images and EEL spectra were acquired in a VG Microscopes HB501UX scanning transmission electron microscope (STEM) operated at 100 kV and equipped with a field emission gun, a parallel EELS and a Nion aberration corrector. Figure 1(a) shows a Z-contrast image of the BCMO sample. From the analysis of these images, no chemical ordering among Bi/Ca cations is present. Simultaneously, EELS can probe the occupancy of the outer d-states of the Mn atoms. The white lines at the L_3 and L_2 absorption edges of transition metals are a characteristic signature of electronic transitions from the $2p_{1/2}$ and $2p_{3/2}$ Mn core states to unoccupied d-like states near the Fermi level. The ratio of the intensity of the L_3 peak to the L_2 peak, the L_{23} ratio, correlates with the formal Mn oxidation number [1, 2]. Figure 1(b) shows the dependence of the L_{23} ratio with the position in the sample when the beam is swept parallel to the pseudo-cubic [100] direction. Clearly, the L_{23} ratio exhibits a modulation with a periodicity varying between 11 and 15 Å. When rotating the scanning direction by 90º no spatial modulation of the Mn L_{23} ratio was observed, which points to a stripe-like geometry for the *3d* occupancy ordering. We will show how CO is basically an ordering within the occupancy of site-specific electronic states, i.e. orbital occupancy.

Another quite remarkable feature found in manganites is the so called phase separation [3]. In such scenario, ferromagnetic metallic (FM) and antiferromagnetic insulating, charge ordered domains would coexist within the same material. It has been suggested that phase separation might be directly connected to the CMR properties of these oxides. We will show studies devoted to map phase separation in ultrathin, epitaxially strained $La_{0.3}Ca_{0.7}MnO_3$ (LCMO) films. As an example, figure 2(a) shows a Z-contrast image of a 6.5 nm LCMO film, and figure 2(b) shows a mapping of the formal Mn oxidation state within the area marked with a rectangle in figure 2(a). The Mn valence oscillates in a non random fashion, showing the presence of clusters where the Mn oxidation state is closer to +3, a few nanometers in size [4]. These nanodomains do not seem to correlate with changes in the O content.

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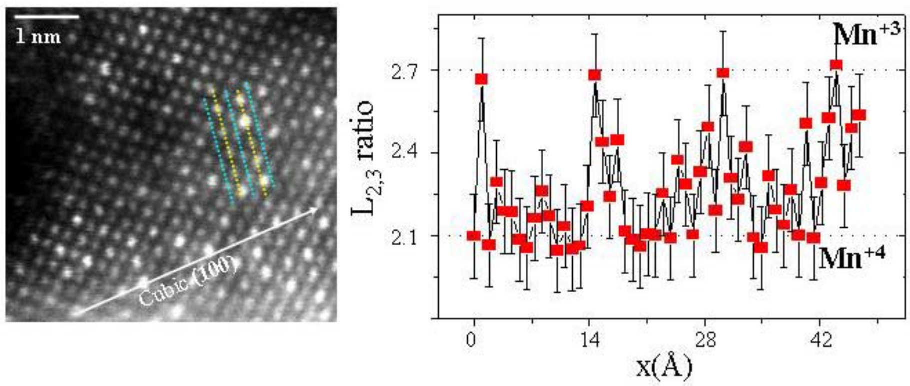

FIG. 1. (a) Z-contrast image of a $Bi_{0.37}Ca_{0.63}MnO_3$ manganite. Blue dotted lines mark the MnO planes, while yellow lines mark the Bi/CaO planes. (b) Dependence of the $L_{2,3}$ ratio, the formal oxidation state of the Mn atoms, with position when scanning the beam along the arrow marked on figure 1(a). Dotted lines mark the expected $L_{2,3}$ ratio of Mn^{+3} (top) and Mn^{+4} (bottom)..

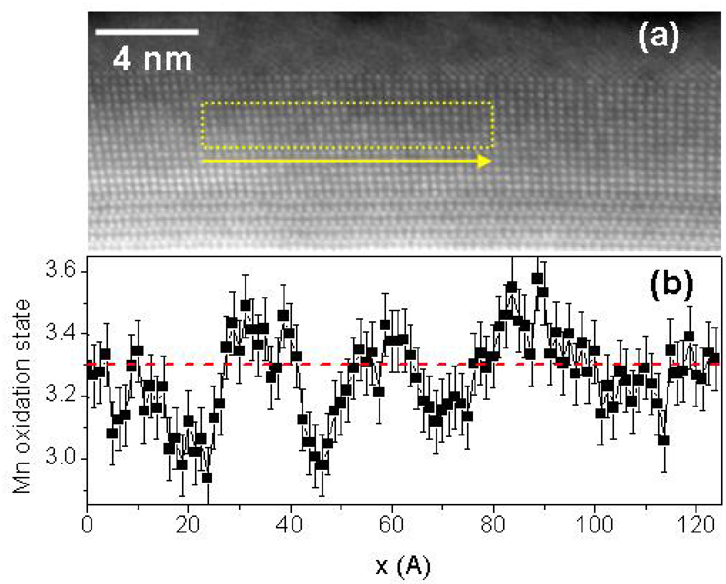

FIG. 2. (a) Z contrast image of an epitaxially strained LCMO film. (b) Mn formal oxidation state, deducted from the L_{23} ratio measured from EELS, along the area marked in yellow in figure 2 (a).

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