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Variable-temperature EELS study of magnetic transitions in $LaCoO_3$ thin films

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The perovskite-oxide $LaCoO_3$ has been studied intensely over the last fifty years due to the two broad transitions in its magnetic susceptibility (T ~ 80 K) and the subsequent nonmetal-metal transition (T ~500 K – 600 K).[1] While the exact origin of the two magnetic transitions in $LaCoO_3$ are still controversial, it is commonly accepted that the spin-state of the Co^{3+}-ions at low temperature (i.e. T < 80 K) is the low spin-state (LS; S=0).[1] However, different models for the Co^{3+} spin-state in the temperature regime between 80 K and 500 K have been proposed.[2] Recently, first-principles calculations have suggested that the occurrence of an intermediate spin-state (IS; S=1) with $t_{2g}^5 e_g^1$ in the temperature between 80 and 500K is responsible for the transition at 80K.[3] We have shown that by using electron energy-loss spectroscopy (EELS) in a transmission electron microscope (TEM),more specifically the O K-edge pre-peak intensity, the spin-state transition of the Co^{3+}-ions can be directly measured and quantified (see Figure 2a).[4]

In addition to suggesting that the intermediate Co^{3+}-ion spin-state is energetically favorable at 300K, Korotin et al.[3] have also suggested that by changing the $LaCoO_3$ lattice parameter, different Co^{3+}-ion spin-states can be stabilized even at low temperatures suggesting that ferromagnetic ordering in $LaCoO_3$ can be achieved. Motivated by these results, we have synthesized fully stoichiometric 30 nm $LaCoO_3$ (001) thin films on $LaAlO_3$ (001). The lattice mismatch between the $LaAlO_3$ support (a=3.789 Å) and the pseudo-cubic unit-cell of $LaCoO_3$ (a_c=3.805Å) should result in a ε=-0.42% lattice compression of the $LaCoO_3$ film. Figure 1a shows an atomic-resolution Z-contrast image of the $LaCoO_3/LaAlO_3$ interface, acquired using the aberration-corrected VG501 at LBNL. The interface appears atomically abrupt and no dislocations have been found at the interface. However, atomic-column resolved EELS shows that significant amounts of Cr are present in the first 3 monolayers of the $LaCoO_3$ films, but not in the $LaAlO_3$ support. The source of the Cr at the interface is currently unclear. Nevertheless, the O K-edge shows that the pre-peak intensity increases to its bulk value within 1-2 monolayers of the $LaCoO_3$ film, indicating a fully stoichiometric film. The Co L-edges have been used to determine the Co-valence state as a function of position, and Co^{3+} is found after the first 2 monolayers. A mixed Co^{3+}/Co^{4+} valence state is found in the first 2 monolayers, where the presence of Cr could affect the Co-bonding or O stoichiometry.

Figure 2a) shows the O K-edge of bulk $LaCoO_3$ as a function of temperature, where the O K-edge pre-peak (labeled *a*) is decreased above the transition temperature as a result of the increased Co^{3+} spin state.[4] The O K-edge and Co L-edge as a function of temperature for the $LaCoO_3$ thin-film are shown in Figures 2b) and 2c). It can be seen that, contrary to bulk $LaCoO_3$, the O K-edge pre-peak intensity (labeled *a*) does not increase at low temperature, but remains unchanged indicating that the Co^{3+} intermediate spin-state has been stabilized at low temperature due to the bi-axial strain. The Co L-edge shows a significant increase in the L_3/L_2 ratio, which can be either due to an increased O vacancy concentration or an increase in the local magnetic moment. However, the increased concentration of O vacancies can be excluded as a potential explanation for the increased Co L_3/L_2 ratio, since the O K-edge fine-structure does not change upon cooling to 94.5 K.

In this presentation, we will discuss our high-resolution EELS study in combination with electron holography and SQUID measurements to determine the potential ferro-magnetic transition in biaxially-strained $LaCoO_3$.[5]

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Figure 1:

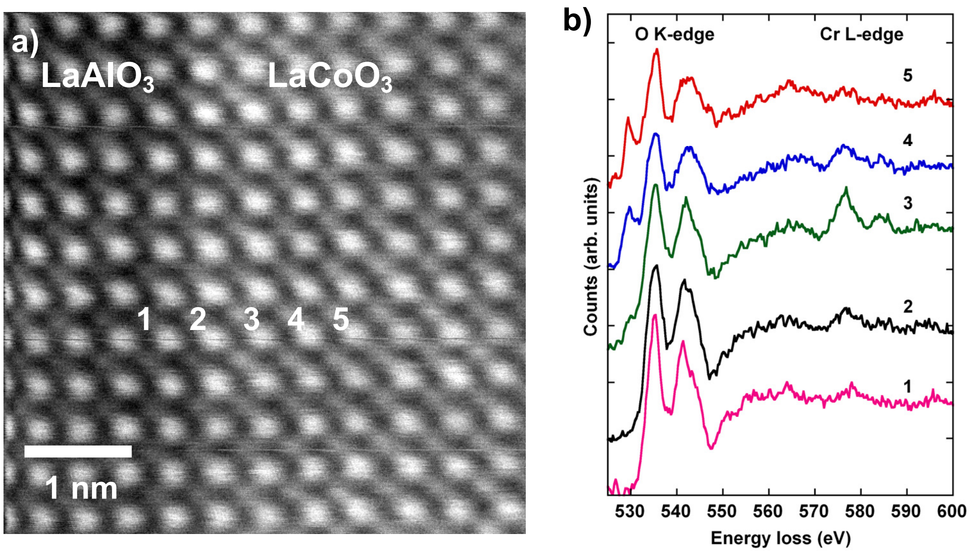

Figure 1: $LaCoO_3$ [001]/$LaAlO_3$ [001]: a) Atomic-resolution Z-contrast image using an aberration-corrected VG501; b) atomic-column resolved EELS showing the O K-edge, as well as the Cr L-edges in the first 3 layers of the $LaCoO_3$ film.

Figure 2:

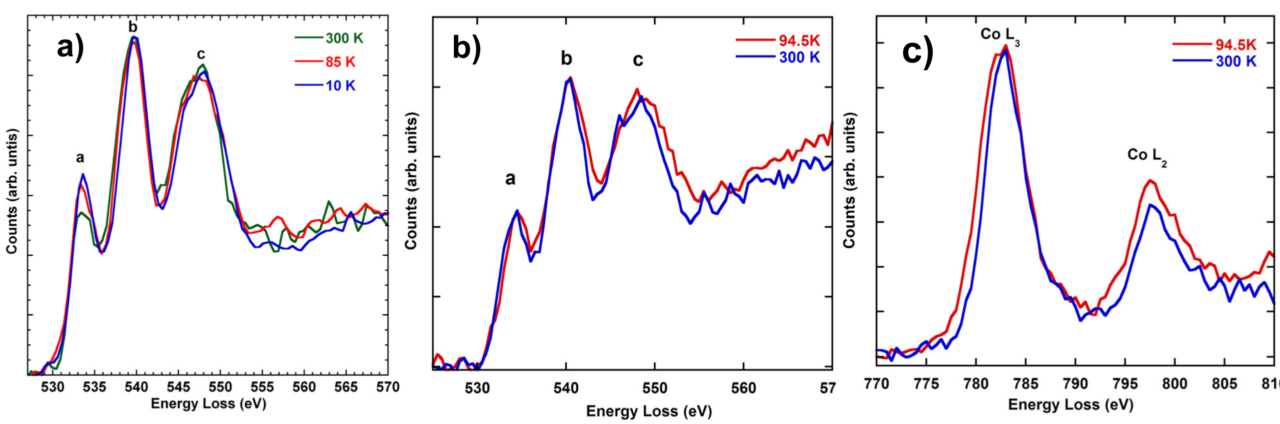

Figure 2: EELS spectra of the O K-edge as a function of temperature for a) bulk $LaCoO_3$, b) the strained $LaCoO_3$ thin-film. c) Co L-edges as a function of temperature for the $LaCoO_3$ thin-film.

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