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Measuring Phase Transitions in $La_{1-x}Sr_xCoO_3$ Using In-Situ Atomic-Resolution Z-contrast Imaging and EELS

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The perovskite oxide $LaCoO_3$ has been studied over the last few decades primarily due to its two transitions, namely the transition from a nonmagnetic insulating state to semiconducting one at 80 K and the transition from semiconducting state to metallic phase above 500 K. While the transition at 80 K is believed to be due to a change in the Co^{3+}-ion spin state from a low spin ($t_{2g}^6 e_g^0 S=0$) to an intermediate spin ($t_{2g}^5 e_g^1 S=1$), the high-temperature transition stems from a change in the Co^{3+}-ion spin-state from the intermediate spin ($t_{2g}^5 e_g^1 S=1$) to the high spin ($t_{2g}^4 e_g^2 S=2$). Previously, it has been shown that epitaxially $LaCoO_3$ films grown on various substrate materials ($LaAlO_3$ or $(LaAlO_3)(Sr_2AlTaO_6)$ substrates) exhibit a ferromagnetic ordering transition at temperatures close to 80 K, which suggests that the biaxial strain induced from the substrate in the $LaCoO_3$ film stabilizes the intermediate Co^{3+}-ion spin state at low temperature [1]. On the other hand, tuning the ferromagnetism of $LaCoO_3$ can be achieved at various temperatures by doping bulk sample with smaller atoms, such as Sr.

In this work, we examine the effect of Sr doping on the magnetic properties of $LaCoO_3$ single crystal samples. More specifically, we utilize a combination of atomic-resolution HAADF and ABF imaging in combination with EELS and in-situ heating and cooling experiments in our aberration-corrected JEOL ARM200CF with a 200 KV cold field-emission electron gun to examine the magnetic and spin-state transitions in $La_{1-x}Sr_xCoO_3$ ($x=0-0.3$) at different temperatures. In-situ cooling experiments are performed using the Gatan double tilt liquid nitrogen cooling holder at 95 K. To study the relationship between magnetic properties and structural characteristics, atomic resolution STEM imaging is used as shown in (Figure 1). With increasing the doping concentration, a change in crystal structure is observed by using annular bright field (ABF) imaging, in particular the distortion of the CoO_6 octahedra. Using energy-loss magnetic circular dichroism (EMCD) [2], we measure the ferromagnetic ordering transition in doped $LaCoO_3$ samples using the Co *L*-edges as a function of temperature and doping concentrations. So far, we have found that the Co L-edges exhibit a dichromatic signal, as well an increased oxygen *K*-edge prepeak as a function of Sr doping concentration (Figure 2). We observe the magnetic ordering with increasing Sr doping and find that for $La_{0.95}Sr_{0.05}CoO_3$, a spin state transition occurs upon cooling the sample below 95 K in the microscope column.

To explore the mechanism behind the Co spin-state transitions of $La_{1-x}Sr_xCoO_3$, we will utilize the magnetic anisotropy of $LaCoO_3$ and use angle-resolved EELS at different crystal orientations with respect to the incident beam directions to differentiate the contribution to the EELS signal from different degenerate orbitals as previously shown by Klie et al.[4] A comprehensive study will be conducted to further decrease the temperature of the in-situ experiments using our new liquid hydrogen stage. This might enable us to study the Co spin-state transitions in samples with low Sr-doping concentrations. Furthermore, we will try to quantify the possible CoO octahedra distortions at low temperature. This work will serve to provide a great opportunity to understand and examine the relationship between the Co-ion spin state transitions and the crystal structure of $La_{1-x}Sr_xCoO_3$. [5]

References:

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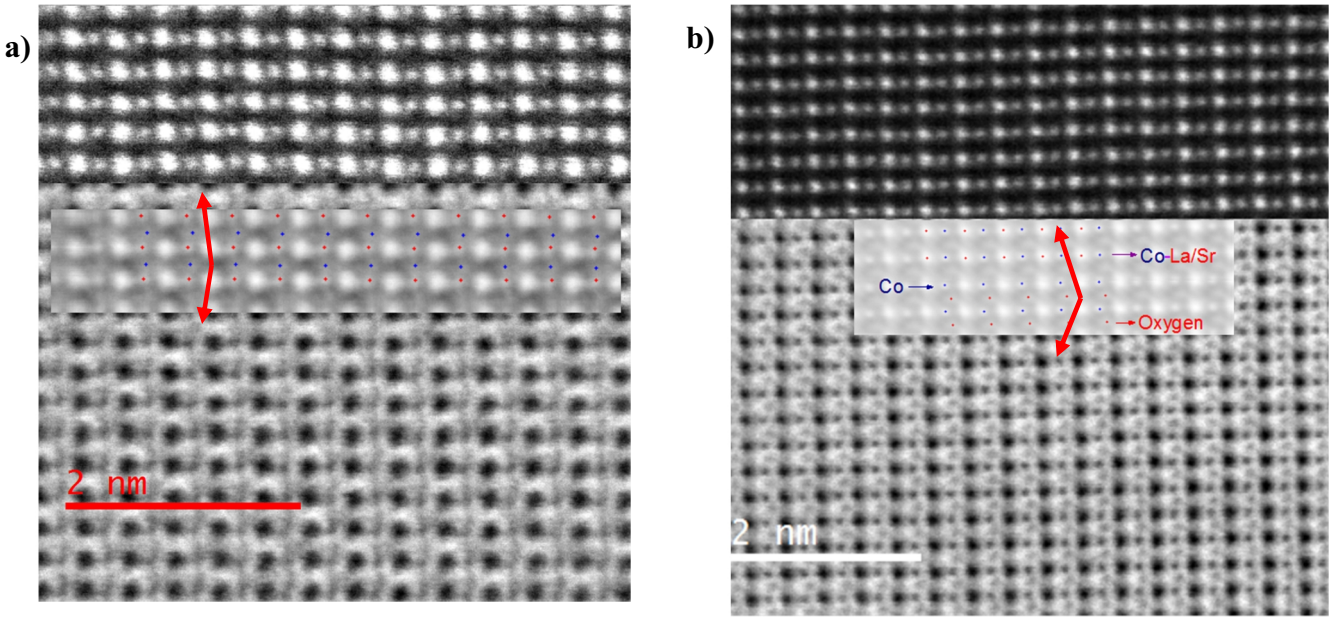

Figure 1: High Angle Annular Dark Field (HAADF) image (at top) and Annular Bright Field (ADF) image (at bottom) of a) $La_{0.95}Sr_{0.05}CoO_3$ and b) $La_{0.7}Sr_{0.3}CoO_3$ sample in (011) direction at room temperature. In the middle, the distortion of oxygen octahedral and the O-Co-O angle is shown with the red arrows which indicates $La_{0.7}Sr_{0.3}CoO_3$ has grater angle.

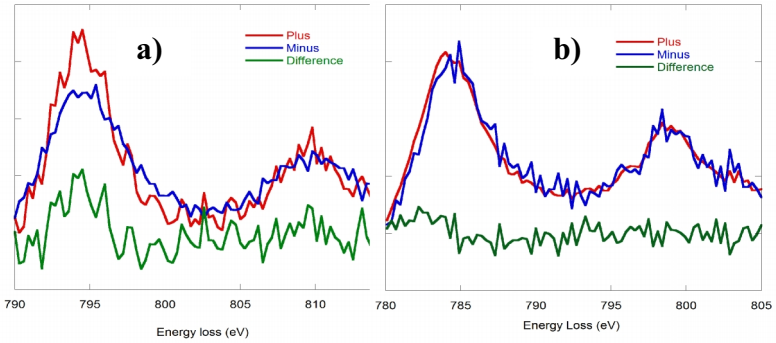

Figure 2: Angular-resolved EELS of a) $La_{0.7}Sr_{0.3}CoO_3$ and b) $La_{0.95}Sr_{0.05}CoO_3$ showing Co L_2 and L_3 edges taken from two different diffraction point namely Plus(+) and Minus(-) at room temperature The difference at Co L edges is an indication of magnetic dichromatism.

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