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In-situ Atomic-Resolution Study of $La_{1-x}Sr_xCoO_3$ Using 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 ($t^{6}_{2g}\ e^{0}_{g}\ S=0$) to an intermediate spin ($t^{5}_{2g}\ e^{1}_{g}\ S=1$), the high-temperature transition stems from a change in the Co^{3+}-ion spin-state from the intermediate spin ($t^{5}_{2g}\ e^{1}_{g}\ S=1$) to the high spin ($t^{4}_{2g}\ e^{2}_{g}\ S=2$). Previously, it has been shown that epitaxially LaCoO3 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 LaCoO3 can be achieved at various temperatures by doping bulk sample with smaller atoms, such as Sr. As Sr doping increases the spin polarons which are caused by substituting divalent Sr^{2+} ions for trivalent La^{+3} ions merge and form short-range FM clusters since the neighboring mixed-valance Co ions interact ferromagnetically via double exchange mechanism [2].

In this work, we examine the effect of Sr doping on the magnetic properties of LaCoO3 single crystal samples. More specifically, we utilize a combination of atomic-resolution HAADF and ABF imaging in combination with EELS and in-situ 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 $La_{1-x}Sr_xCoO_3$ *($x=0.05$-0.3)* at different temperatures. In-situ cooling experiments are performed using the Gatan double tilt liquid nitrogen cooling holder.

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) [3], 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 $La_{0.95}Sr_{0.05}CoO_3$ an increase in O K edge prepeak occurs upon cooling the sample to the liquid nitrogen temperature in the microscope column. as the crystal structure is saved which suggests a spin state transition as reported earlier in NMR experiments [5] as shown in (Figure 2). Changes in the O K prepeak intensity and Co white line ratio are mapped in critically doped $La_{0.83}Sr_{0.17}CoO_3$ at high spatial resolution, suggesting and inhomogeneous spin state distribution, stoichiometry and short-range FM clusters as previously predicted [2, 5].

To explore short-range FM clusters at room temperature and its change through the in-situ cooling process, a comprehensive study including spatially-resolved EMCD, and O Keand Co L edge mapping will be conducted. Furthermore, we will quantify the possible CoO_6 octahedral distortions at low temperature and explore the correlation between the spin states of Co and the octahedral distortion [6].

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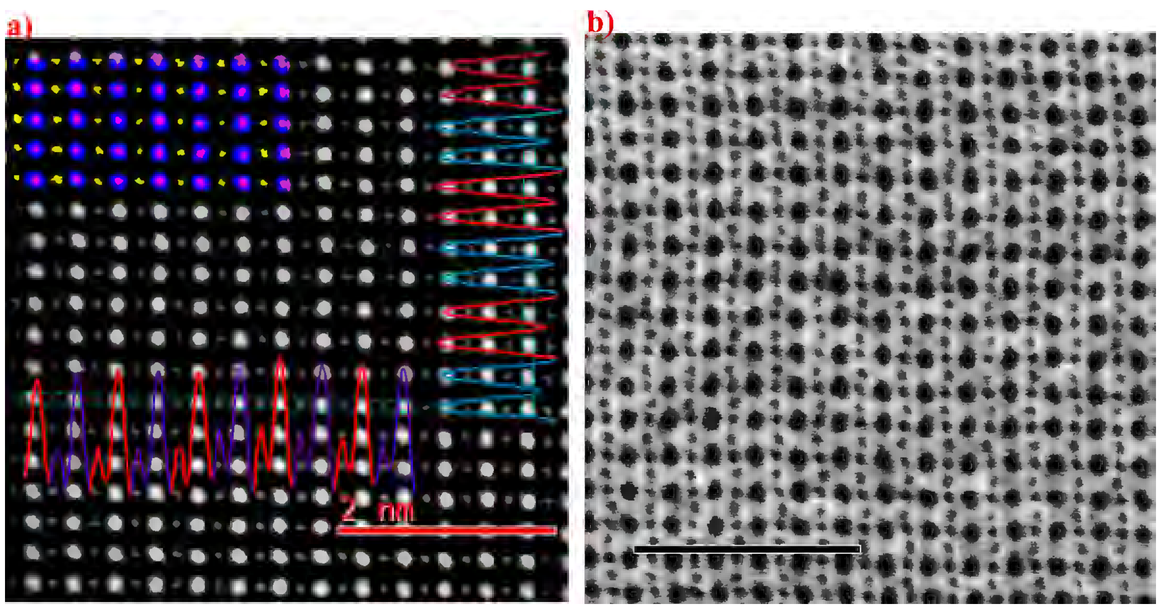

Figure 1: ***a)*** High Angle Annular Dark Field (HAADF) image where the brighter spots are La/Sr columns and weaker ones are Co atoms of $La_{0.95}Sr_{0.05}CoO_3$ in (011) direction at room temperature. Intensity line profile in two directions shows the pairing of neighboring atoms. ***b)*** The ABF image of the same area can resolve the Oxygen columns and the distortion of oxygen octahedral

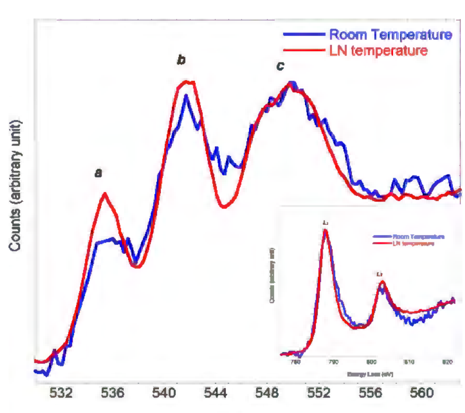

Figure 2 O K edges and Co L edges of $La_{0.95}Sr_{0.05}CoO_3$ are shown at both room temperature and Liquid nitrogen temperature. The increase in O K edge prepeak, labeled as ***a,*** as no change in Co white line ratio through in situ cooling suggests a spin state transition

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