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Meeting-report

Mapping Lattice Distortions Across Phase Transitions With Atomic-Resolution STEM

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I had the privilege of learning from Lena as a graduate student at Cornell. During those years Lena's enthusiasm and dedication to uncovering the physics of materials through cutting-edge electron microscopy was a constant motivating force. My research under her mentorship focused on mapping picometer- to Ångström-scale atomic distortions in a wide variety of functional materials. This was one of many areas in which Lena's work had a significant impact. She pushed the limits of measuring lattice distortions linked to connections between charge, spin, lattice, and orbital degrees of freedom in quantum materials and expanded the technique to cryogenic and intermediate temperatures, enabling direct visualization of temperature-driven phase transitions [1-3]. One analysis method that has been particularly impactful is the extraction of picometer-scale periodic lattice distortions (PLDs) using atomic column fitting and comparison to a reference lattice generated by damping the modulation of interest from the atomic-resolution image FFT [1]. Since this technique requires selection of distinct sets of Fourier peaks to produce the reference image, it has the potential to extract distortions related to different phases in crystals with phase coexistence.

To demonstrate this ability, we chose $LaNiO_{3-\delta}$ as a model system. While $LaNiO_3$ has a mundane reputation as the only rare earth nickelate that does not exhibit electronic or magnetic transitions, oxygen deficient compounds have shown more complicated electronic and magnetic behavior. As the oxygen vacancy concentration, δ, is increased from 0 to 0.5, the crystal undergoes a metal-to-insulator transition, and for $\delta = 0.25$ and 0.5, it is ferro- and antiferromagnetic, respectively, at low temperature. These property changes are linked to regions of ordered oxygen vacancies, which tend to coexist over length scales of hundreds of nanometers. This phase coexistence makes analysis of the structure and properties of the vacancy-ordered phases very difficult.

By identifying the peaks in an image FFT that are associated with each phase and separately mapping them using the above atomic displacement mapping technique, we identified the cation displacement patterns in the $LaNiO_{2.5}$ and $LaNiO_{2.75}$ phases as shown in figure 1. The extracted displacement patterns confirm the previously published structure for the $\delta = 0.5$ phase [4] and elucidate the cation displacements for the $\delta = 0.25$ phase for the first time. The extraction of real space lattice distortions in heterogeneous crystals enabled by this analysis is relevant to a variety of functional oxides, nitrides, and more across the fields of energy materials, multiferroics, and quantum materials.

This work during my doctoral studies continues to play an important part in my investigation of conductance switching mechanisms in candidate materials for neuromorphic computing. These switching mechanisms often leverage metal-to-insulator or spin transitions that are concomitant with subtle distortions in the atomic lattice. The spin transition in cobalt oxides has been a recent focus of our efforts [5]. I will show how we used atomic column mapping, in combination with electron energy loss spectroscopy (EELS), to characterize its spin transition upon in-situ heating. Direct visualization of the heating-induced lattice distortions and the heterogeneity therein inform our understanding of the transformation mechanism and suggest directions for further material development [6].

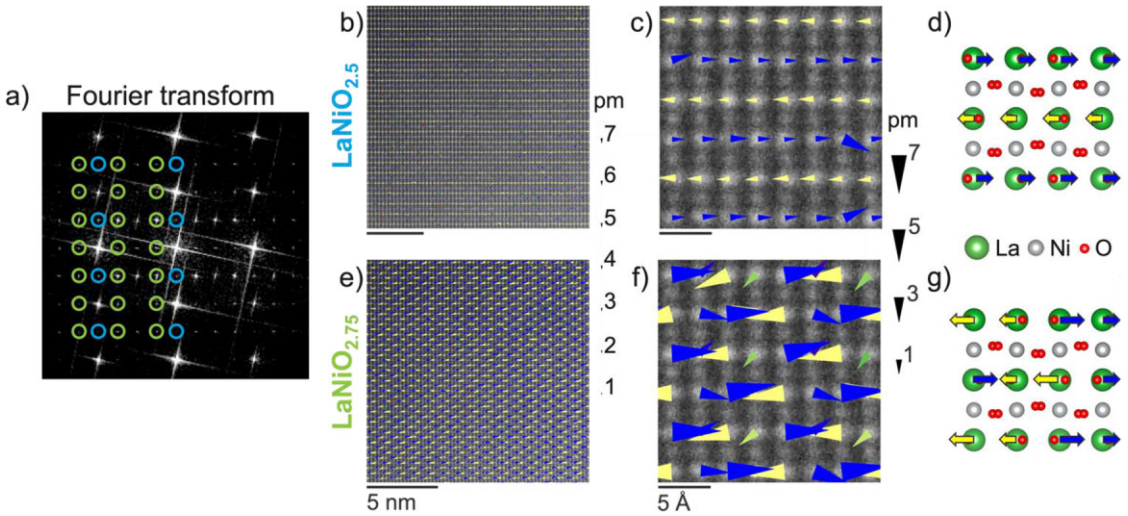

Fig. 1. Atomic column displacements mapped for La along the $[110]_{pc}$ projection of $LaNiO_{3-d}$. (a) FFT of the HAADF-STEM image shown in b and e, where the peaks circled in blue and green correspond to the d = 0.5 and 0.25 phases, respectively. (b,e) Displacements associated with the d = 0.5 and 0.25 phases, respectively, over a ~15 nm field of view. A subset of b(e) is presented in c(f), more clearly displaying the displacement pattern. An atomic model of $[110]_{pc}$-oriented $LaNiO_3$ is shown in d and g overlaid with arrows indicating the displacement patterns for the d = 0.5 and 0.25 phases. The arrow size indicates the magnitude, and the arrow direction and color indicate the direction of the displacement for each atomic column.

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