

## Channeling-Induced Artifacts in Atom Tracking of Cations in Distorted Perovskites Imaged by HAADF-STEM

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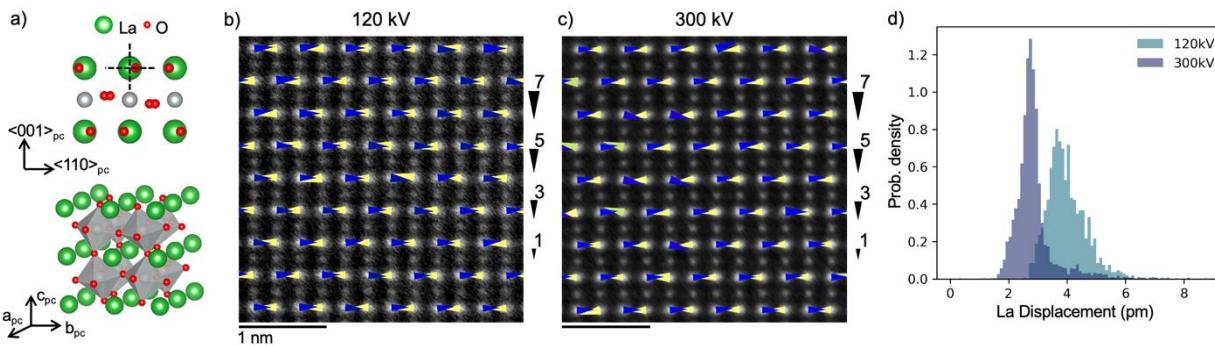
Aberration-corrected STEM imaging has become an immensely powerful tool for studying the atomic structure of quantum materials. Subtle atomic displacements that dictate how these materials function can now be quantified at the picometer scale thereby providing a real-space picture of ferroelectric order, periodic lattice distortions, etc. [1,2,3]. Combined with other STEM modalities, the connection between lattice, spin, charge, and orbital degrees of freedom can be probed. High-angle annular dark-field (HAADF) STEM imaging is commonly used for lattice displacement measurements. Due to its strong Z dependence, HAADF-STEM imaging is often assumed to be insensitive to light atoms such as oxygen. In columns containing a mixture of heavy and light atoms, however, channeling of the electron beam, long known to strongly affect the measured HAADF signal [4], is influenced by the light as well as the heavy atoms. Here, we show experimentally that cation sites in a distorted perovskite oxide crystal imaged by HAADF-STEM appear displaced by several picometers with respect to their true lattice positions, caused by coherently displaced oxygens in the same atomic columns. We elucidate the origin of these apparent displacements using multislice simulations and consider ways to avoid or mitigate the effects.

In Fig. 1b and c, we show HAADF-STEM images of rhombohedral  $\text{LaNiO}_3$ , acquired using 120 and 300 kV accelerating voltages, respectively, viewed down the  $\langle 110 \rangle$  pseudocubic zone axis. Overlaid arrows represent the measured displacements of the lanthanum-oxygen columns with respect to the expected crystallographic positions of the lanthanum atoms. Note that the displacement pattern matches that of the oxygens in the atomic model shown in Fig. 1a, and the displacement magnitude changes with voltage. The maxima of the magnitude distributions shown in Fig. 1d are 3.7 and 2.8 pm for 120 and 300kV, respectively.

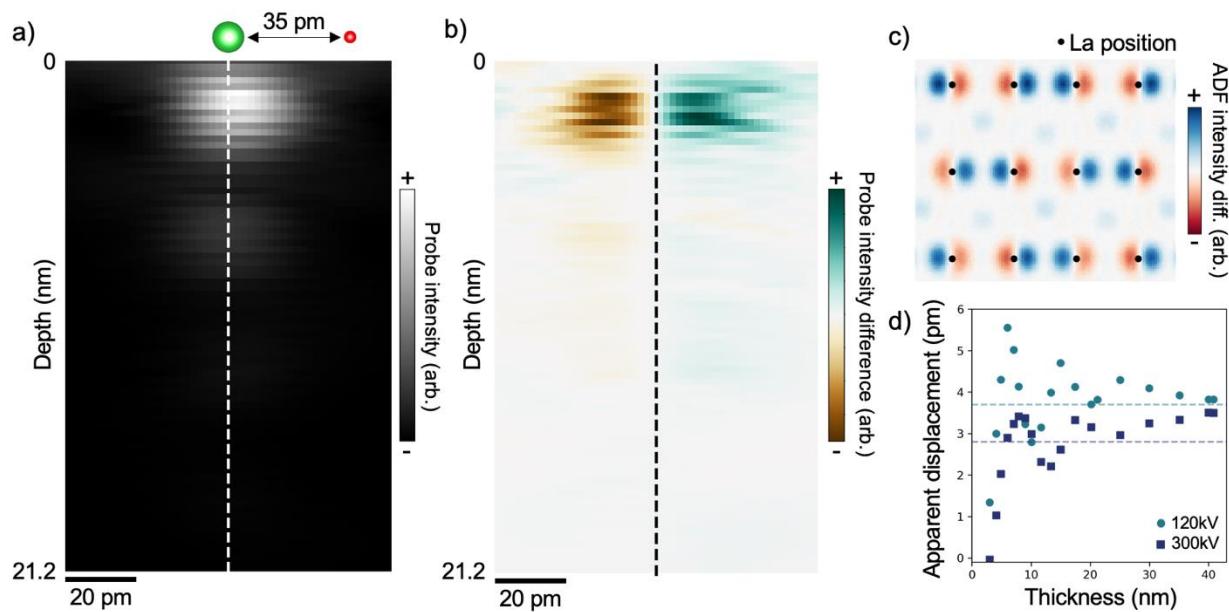
To understand the origin and dependencies of the apparent displacements of the lanthanum-oxygen columns, we simulate the electron wavefunction propagation and resulting HAADF-STEM images for  $\langle 110 \rangle$  oriented  $\text{LaNiO}_3$  using the multislice algorithm [5]. We first simulate the wavefunction propagation for a probe positioned on a lanthanum column as indicated by the crosshairs in Fig. 1a. A cross section of the resulting probe intensity as a function of depth is shown in Fig. 2a, where the dotted white line represents the initial probe position and the positions of the lanthanum and oxygen atoms in the column are shown at the top. Fig. 2b shows the difference between the probe intensity cross section in Fig. 2a and the perpendicular cross section where the lanthanum and oxygen atoms are aligned horizontally with respect to the plane of the cross section. This difference map shows a significant probe intensity shift toward the oxygen atoms within the first 5 nm of the sample, followed by oscillations in the intensity characteristic of channeling. To visualize the effect of this shift in probe intensity on the resulting HAADF signal, we simulate images of the  $\text{LaNiO}_3$  crystal with and without oxygens included.

The difference between those simulated images is plotted in Fig. 2c and shows that the oxygens cause an increase in the scattering signal toward the oxygens and away from the lanthanum positions (indicated by black dots). We quantify the displacement of the lanthanum-oxygen column positions in the simulated HAADF-STEM images with respect to the true lanthanum position as a function of thickness in Fig. 2d. This plot shows that the apparent displacements increase sharply with thickness initially and then oscillate in accordance with the channeling signal before flattening out at a thickness of ~40 nm.

While the magnitudes of the apparent displacements (~3-5 pm) are significantly less than the true oxygen displacements (35 pm), they are on the order of displacements expected for periodic lattice distortions in materials such as charge ordered manganites [2,3]. The ability of light oxygen atoms to affect the apparent positions of cations in HAADF-STEM images is therefore crucial to consider when attempting to quantify the lattice distortions in such systems. In some crystals, a zone axis can be chosen such that oxygen atoms are not coherently displaced in mixed cation/anion columns, thus avoiding the effect. In other crystals, symmetry dictates that there are no zone axes containing coherently displaced oxygen atoms. If a measurement requires imaging of a zone axis containing coherently displaced oxygens, however, we find that the apparent displacements of cation columns caused by channeling due to oxygens can be reduced by imaging at an increased voltage. For example, Fig. 2d shows the apparent displacement versus thickness for 300 kV in addition to 120 kV, showing that at nearly every thickness, the apparent displacement is lower for 300 kV. This result is confirmed by experiment in Fig. 1c,d where the apparent lanthanum displacements are overlaid on an image acquired at a 300 kV accelerating voltage and the corresponding displacement magnitude distribution shows a lower average value than for the image acquired at 120 kV. Thus, the positions of oxygen atoms should be carefully considered when performing atom tracking analyses on any image with mixed cation/anion atomic columns, even in Z contrast images [6].



**Figure 1.** (a) Crystal structure of LaNiO<sub>3</sub> showing oxygens displaced with respect to the lanthanum atoms in the <110><sub>pc</sub> projection. (b,c) HAADF-STEM images acquired at 120 and 300 kV accelerating voltages, respectively, with overlaid arrows representing the measured displacements of lanthanum-oxygen atomic columns with respect to the crystallographic positions of the lanthanum atoms. (d) Distributions of apparent lanthanum-oxygen column displacements at 120 and 300 kV. Distribution maxima occur at 3.7 and 2.8 pm, respectively.



**Figure 2.** (a) Cross section of the simulated probe intensity as a function of crystal depth for a probe centered on a lanthanum column. The white dashed line represents the initial probe position, and the lanthanum and oxygen positions are shown at the top. (b) Difference between the probe intensity cross section in (a) and the perpendicular cross section in which the lanthanum and oxygen atoms line up horizontally when projected onto the plane. The difference map shows a clear shift in probe intensity toward the oxygen atoms as the electron beam propagates through the crystal. (c) Difference between simulated HAADF-STEM images of  $\text{LaNiO}_3$  with and without oxygen atoms included, showing the oxygen atoms cause a shift in the HAADF signal off the crystallographic lanthanum positions and toward the oxygens. (d) Simulated lanthanum displacement as a function of crystal thickness for accelerating voltages of 120 and 300 kV, showing that a higher accelerating voltage reduces the apparent lanthanum displacements for nearly every thickness. The experimentally measured displacement magnitudes are indicated by a dashed line for each voltage.

## References:

- [1] G. Catalan, et al., *Nat. Mater.* **10** (2011), p. 963.
- [2] I. El Baggari, et al., *Proc. Natl. Acad. Sci. U.S.A.* **115** (2018), p. 1445.
- [3] B.H. Savitzky, et al., *Nat. Comm.* **8** (2017), p. 1883.
- [4] P. Voyles, et al., *Ultramicroscopy* **96** (2003), p. 251.
- [5] E.J. Kirkland, et al., *Ultramicroscopy* **23** (1987), p. 77.
- [6] This work was supported by NSF (DMR-1719875, DGE-1650441, DMR-2039380). Work performed at Argonne National Laboratory (crystal growth and post-annealing studies) was sponsored by the U.S. DOE, Office of Science, Basic Energy Sciences, Materials Science and Engineering Division.