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Three-Dimensional Imaging of Single La Vacancies in $LaMnO_3$

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Non-rigid registration (NRR) of a series of aberration-corrected HAADF STEM images can create images with extremely high signal to noise ratio and enable sub-picometer precision measurements of atom positions [1]. Such images allow us to measure the picometer-level structural changes caused by point defects in HAADF STEM experiments. Here we report an approach for three-dimensional imaging of single La vacancies in $LaMnO_3$ by combining high precision HAADF STEM experiments with frozen phonon simulations and a Bayesian statistical model.

In this study, we investigated $LaMnO_3$ film grown on $DyScO_3$ substrate by molecular beam epitaxy with ~1% composition control. Experiments were conducted on a probe-corrected FEI Titan STEM at 200 kV. The probe convergence semi-angle and detector inner collection angle are 24.5 mrad and 84.4 mrad, respectively.

Figure 1 (a) shows a HAADF STEM image of [100] $LaMnO_3$ created by NRR and averaging of 200 frames. The La columns were fitted to 2D Gaussians to calculate the column intensities and positions. One La vacancy candidate was found in the center of the white box area. Figure 1 (b) is the intensity map of the white box area and the center column (marked as V) has a 6.36% intensity reduction (defined as visibility) compared with surrounding eight La columns. Figure 1 (c) shows the contraction of the surrounding columns toward V. The distance between column B and column D, along x-axis and defined as S1, is reduced by 6.45 pm. The distance between column A and column C, along y-axis and defined as S2, is reduced by 5.40 pm. The sample thickness is 7 nm, measured by position averaged convergent beam electron diffraction [2].

Figure 2 is frozen phonon simulation results using a 7 nm thick $LaMnO_3$ model which contains a single La vacancy, with a structure derived from *ab initio* simulations. Figure 2 (a) shows the visibility as a function of La vacancy depth, and Figure 2 (b) shows ΔS1 and ΔS2 as a function of La vacancy depth. The depth dependence of these signals arises from probe channeling, and it enables us to localize the vacancy perpendicular to the plane of Figure 1.

We have combined the visibility, ΔS1, and ΔS2 along with the statistical uncertainties in the experiments and simulations into a Bayesian statistical model that calculates the probability that a La vacancy exists in a particular column, and the most probable vacancy depth. Considering ΔS1 and ΔS2 in addition to the visibility enables us to distinguish vacancies inside the TEM sample from vacancies or steps on the sample surface that have different ΔS1 and ΔS2. As shown in Figure 3, the model finds that the column V in Figure 1 (b) contains a single La vacancy with a probability larger than 99% and the most possible position of that vacancy is the third atomic layer in from the entrance surface with a probability of 60%. Automated image analysis and application of the Bayesian model will enable characterization of vacancy distribution and clustering.

Reference:
[1] A.B. Yankovich, *et al.*, Nat. Commun. 5 (2014) 4155.
[2] J.M. Lebeau, *et al.*, Ultramicroscopy. 110 (2010) 118–25.
[3] This work was supported by the US Department of Energy, Basic Energy Sciences, Grant DE-FG02-08ER46547.

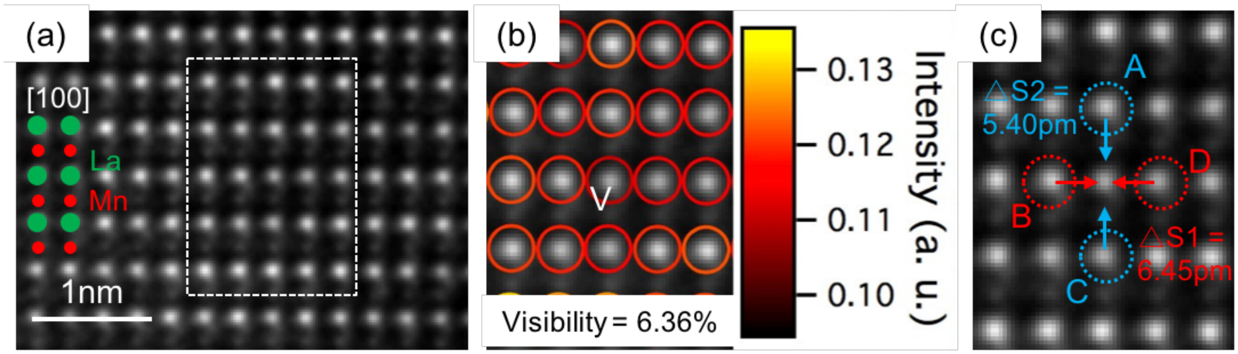

Figure 1. (a) HAADF STEM image of $LaMnO_3$ averaged using 200 frames. (b) Intensity map of the white box area in (a) and the visibility of column V is 6.36%. (c) Inter-column distances around V (S1 and S2) are reduced by 6.45 pm and 5.40 pm, respectively. The sample is 7 nm thick.

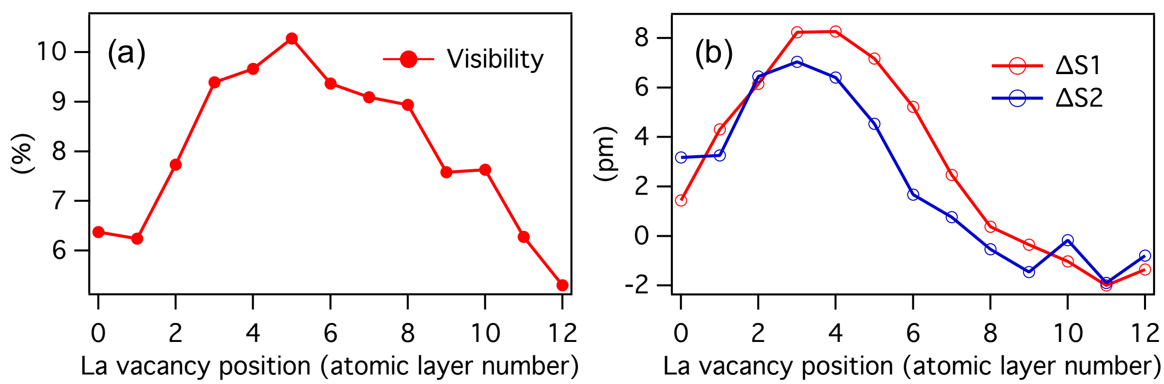

Figure 2. Frozen phonon simulation results for a 7 nm thick sample. (a) visibility of a La vacancy as a function of vacancy depth. (b) ΔS1 and ΔS2 for a La vacancy as a function of vacancy depth.

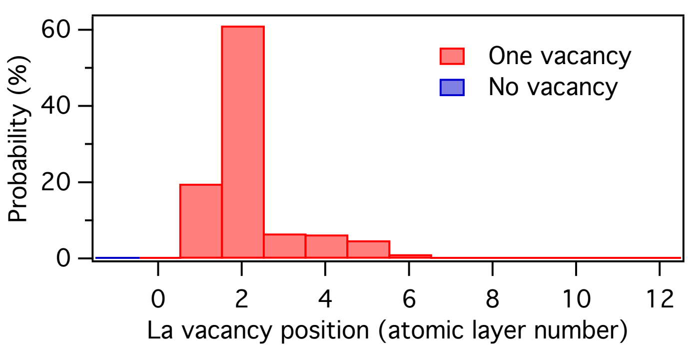

Figure 3. Single La vacancy position probability calculated by Bayesian model. The probability of no vacancy existing is smaller than 0.1%. The most possible position of the vacancy is the third layer with a probability of 61%.