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Bayesian Statistical Model for Imaging of Single La Vacancies in $LaMnO_3$

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Previous simulation studies have demonstrated that single La vacancies can be detected using high precision quantitative high-angle annular dark-field (HAADF) Z-contrast scanning transmission electron microscopy (STEM) [1] by both the reduction in scattered intensity created by the missing atom and the distortion of the surrounding atom positions [2]. We have now experimentally detected single La vacancies on nominally stoichiometric $LaMnO_3$ films grown on $DyScO_3$ substrate by molecular beam epitaxy with ~1% control of cation stoichiometry. The vacancy depth is determined from channeling behavior of the electron probe, quantified by a Bayesian statistical model that compares experiments to a library of simulations

Figure 1 (a) is an experimental high-precision quantitative HAADF STEM image of $LaMnO_3$ along [100]. The TEM sample thickness is 6.5 nm. A simulated image at the same specimen thickness and collection angle is in the white dashed box. For each La-O column, we studied its visibility (V) and inter-column separation changes (ΔS_1 and ΔS_2) [2]. For column A, marked in (a), V = 10.6%, ΔS_1 = 3.9 pm, and ΔS_2 = 3.0 pm. Figure 1 (b) and (c) are simulated V and simulated ΔS_1 and ΔS_2 for a 6.5 nm TEM specimen, respectively. If we consider a conservative uncertainty band twice the estimated experimental intensity uncertainty of 1%, the visibility is consistent with a vacancy anywhere from 1.1 to 5.2 nm deep in the sample. ΔS_1 and ΔS_2, given an uncertainty of 1 pm, indicate the vacancy is either 0 – 0.8 nm deep or near 3.5 nm deep. The overlap of all three factors localizes the vacancy to 3.4 to 4.2 nm deep into the sample. Figure 1 (d) shows the Bayesian statistical model calculation results on column A that the probability it contains a single La vacancy is greater than 99.9%, and the most probable depth (65% probability) is 3.5 nm (the 7th atomic layer).

In order to validate the Bayesian statistical model, we have done a series of phantom tests. In each test, fake experimental measurements were created by adding noise to the noiseless simulated V, ΔS_1, and ΔS_2 from a specific $LaMnO_3$ model. Then we tested whether the Bayesian model correctly recovered whether or not a La vacancy was present and the depth of the vacancy if it was present. The noise was drawn from a normal distribution with mean value of 0, standard deviation of 1% for V, and 1 pm for ΔS_1 and ΔS_2. Each test was repeated with 10000 different noise realizations.

Figure 2 is a contour plot of the phantom test results with the real vacancy depth in the model on the *x* axis and the Bayes model result on the *y* axis. For example, the Bayesian model predicted that there is no La vacancy in the model in all 10000 tests from the $LaMnO_3$ model without a vacancy. For a single vacancy $LaMnO_3$ model with the vacancy at 2.4 nm depth, the Bayes model found the vacancy at the correct depth in 61% tests, 38% tests had a 1-layer prediction error and only <1% test had a 2-layer error. If only ±1 layer prediction uncertainty is allowed, the precision is higher than 85% in most cases when the vacancy depth is smaller than 7 nm. This demonstrates that the vacancy depth calculated by the Bayesian model is very reliable and the Bayesian model is able to precisely locate a single La vacancy up to 7 nm deep with ±1 layer uncertainty [3].

References:

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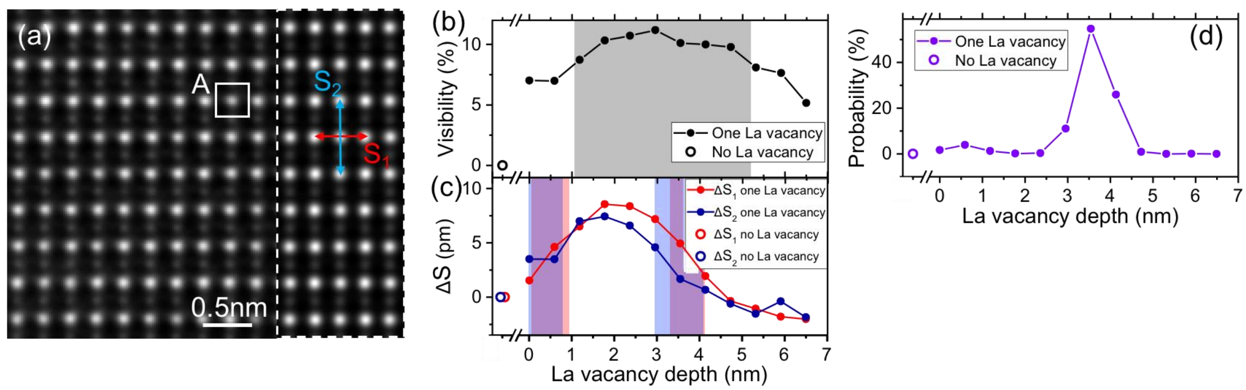

Figure 1. (a) HAADF STEM image of LaMnO3 along [100]. (b) and (c) Simulated visibility and simulated ΔS_1 and ΔS_2 for a TEM specimen of the same thickness. (d) Probability for the vacancy position calculated by the Bayesian model.

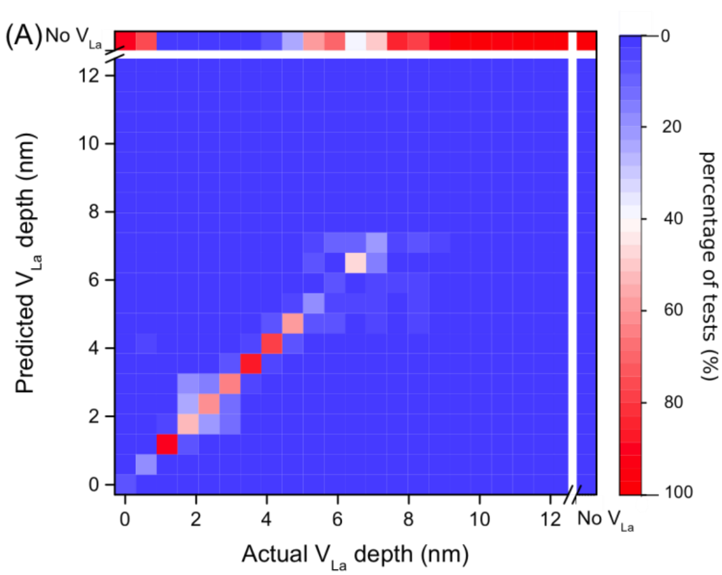

Figure 2. Phantom tests on the Bayesian statistical model on 12 nm $LaMnO_3$ model. Predicted La vacancy depth *vs.* the actual La vacancy depth.

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