
S.D. Findlay¹, Z. Chen², M. Weyland³⁴, X. Sang⁵, W. Xu⁵, J.H. Dycus⁵, J.M. LeBeau⁵ and L.J. Allen⁶

¹. School of Physics and Astronomy, Monash University, Melbourne, Australia.
². School of Applied and Engineering Physics, Cornell University, Ithaca, USA.
³. Monash Centre for Electron Microscopy, Monash University, Melbourne, Australia.
⁴. Department of Materials Science and Engineering, Monash University, Melbourne, Australia.
⁵. Department of Materials Science and Engineering, North Carolina State University, Raleigh, USA.
⁶. School of Physics, University of Melbourne, Melbourne, Australia.

In analytical electron microscopy, energy dispersive X-ray spectroscopy (EDX) has long been able to assess elemental composition on the micron scale, measuring elemental concentration ratios with a sensitivity approaching a few atomic percent [1]. Improvements in detector design and source brightness have achieved EDX mapping in scanning transmission electron microscopy (STEM) at atomic resolution [2]. However, relative concentration may be less informative than the absolute number of atoms at this scale, where structures of interest include nanoparticles and crystal defects. Counting atoms was achieved in high-angle annular dark-field STEM imaging through absolute scale comparison between experiment and simulation [3]. Is this feasible in atomic resolution STEM EDX?

The number of X-ray counts \( N \) is given by

\[
N(R) = ITF_{\text{ion}}(R, t, X_{\text{abs}}) \omega \left( \frac{\Omega}{4\pi} \right) D_{\text{eff}} \quad (1)
\]

with \( R \) the probe position, \( I \) the beam current, \( T \) the probe live dwell time, \( F_{\text{ion}} \) the fraction of incident electrons causing ionization events (depending on probe-position, thickness and electron scattering through the material; a correction for X-ray absorption \( X_{\text{abs}} \) can also be included), \( \omega \) the fluorescence yield, \( \Omega \) the detector solid angle, and \( D_{\text{eff}} \) the detector efficiency [4]. Absolute scale comparison between experiment and theory thus has two aspects: (i) characterising the experimental geometry and (ii) simulating electron scattering through the crystal [4,5].

First proof-of-principle work achieved good agreement in absolute scale comparison between experiment and simulation for the mean EDX signal through careful characterization of the experimental geometry, but had insufficient count rate to form atomic resolution images [4]. Using an FEI Titan G2 at 200 keV with a four windowless silicon-drift detector (SuperX) system, subsequent work showed good quantitative agreement at atomic resolution, albeit after repeat-unit averaging in crystalline SrTiO₃ [5]. Figure 1 shows 2D maps at select thicknesses, and plots of the peak, mean and minimum signals for several thicknesses (peak and minimum counts are averages within a 0.1 nm radius of the atomic column and minimum positions, respectively). Some discrepancies are evident, and possible causes will be discussed [6].

We thank Dr A.J. D’Alfonso and Mr Daniel Taplin for contributions to this work. This research was supported under the Australian Research Council's Discovery Projects funding scheme (Project DP140102538). XS, WX, JHD, and JML gratefully acknowledge the Air Force Office of Scientific Research (FA9550-14-1-0182) for support of this research and also acknowledge the Analytical Instrumentation Facility (AIF) at North Carolina State University, which is supported by the State of North Carolina and the National Science Foundation. JHD acknowledges support for this work by the National Science Foundation Graduate Research Fellowship (Grant DGE-1252376).

Figure 1. Quantitative comparison of experimental and simulated EDX signals for the Sr K, Ti K, and Sr L-shell peaks. Left: STEM images for thicknesses 15.6 nm and 28.1 nm. The probe-forming aperture semiangle is 19.5 mrad. The simulations include a Gaussian effective source distribution with full-width-half-maximum 0.21 nm. The scale bar applies to all images. Right: Peak, mean and minimum X-ray counts as a function of sample thickness, comparing experiment (symbols) and simulation (lines). The experimental error bars represent only the error arising from counting statistics.