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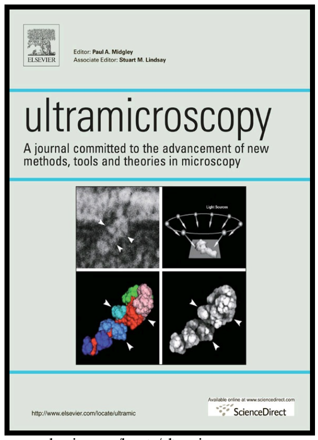

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Quantitative atomic resolution elemental mapping via absolute-scale energy dispersive X-ray spectroscopy

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Abstract

Quantitative agreement on an absolute scale is demonstrated between experiment and simulation for two-dimensional, atomic-resolution elemental mapping via energy dispersive X-ray spectroscopy. This requires all experimental parameters to be carefully characterised. The agreement is good, but some discrepancies remain. The most likely contributing factors are identified and discussed. Previous predictions that increasing the probe forming aperture helps to suppress the channelling enhancement in the average signal are confirmed experimentally. It is emphasised that simple column-by-column analysis requires a choice of sample thickness that compromises between being thick enough to yield a good signal-to-noise ratio while being thin enough that the overwhelming majority of the EDX signal derives from the column on which the probe is placed, despite strong electron scattering effects.

Keywords:
Scanning transmission electron microscopy (STEM), energy dispersive X-ray (EDX) spectroscopy, atomic-resolution mapping, elemental quantification.

1. Introduction

Atomic resolution elemental mapping via energy dispersive X-ray (EDX) spectroscopy in scanning transmission electron microscopy (STEM) was achieved in 2010 [1–3]. Like the long-established high-angle annular dark field (HAADF) imaging mode, STEM EDX images are directly interpretable for qualitative analysis [4–6]. Also like HAADF [7], quantitative analysis of STEM EDX images requires accounting for the strong dynamical scattering, also called channelling, of the electron probe. The consequences of channelling for two-dimensional (2D) maps can be broadly grouped into two categories: changes in the relative contrast and changes in the absolute-scale intensity. The former issue has been explored by Kothleitner *et al.* [8], who demonstrated good quantitative agreement between experiment and channelling-based simulations in the relative signal on different columns, even when, due to channelling, these ratios bear little resemblance to the true stoichiometry. Good agreement in relative contrast between simulation and experiments is also evident in the work of Forbes *et al.* [9] and Dycus *et al.* [10]. The issue of the absolute-scale of the signal was explored by Chen *et al.* [11], who demonstrated good agreement between experiment and simulation in the total number of X-ray counts recorded for an atomically-fine STEM probe scanned across a $SrTiO_3$ specimen. The present paper unifies these two approaches, demonstrating absolute-scale comparison between experiment and simulation for atomic-resolution 2D EDX mapping.

Sufficient signal-to-noise to enable good quality atomic resolution 2D EDX maps is achieved here using a system with multiple, large-area, silicon-drift detectors (SDD) [4, 6, 12]. The increased complexity of this detector geometry necessitates accurate numerical modelling to determine effective detector solid angle and X-ray absorption in both the specimen and holder [13, 14]. Achieving good signal-to-noise for 2D images is more challenging than for scan-averaged spectra, especially from very thin specimens. While this can nominally be compensated for by using thicker samples, this may reduce the reliability of interpreting the signal on a column-by-column basis, since dynamical electron scattering can spread the probe appreciably beyond the column on which it is placed [15–17]. Here, experimental and simulation results are combined to produce some sense of the thickness range giving both reasonably good signal-to-noise and tolerably justifying simple column-by-column analysis.

2. Methods

2.1. The experiment and materials

EDX measurements were taken on an FEI Titan G2 with a probe aberration corrector (DCOR, CEOS GmbH) operated at 200 keV. The EDX detection system comprises four windowless silicon-drift detectors (SuperX) giving a large collection solid angle, nominally 0.7 sr [18, 19] though, as discussed in Sec. 2.2, the present analysis uses values calculated via the