Implications of Channeling for Quantitative Energy Dispersive X-ray Spectroscopy in Atomic Resolution Scanning Transmission Electron Microscopy

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Analytical electron microscopy has long been capable of determining elemental concentration ratios to ~1% sensitivity in microanalysis, i.e. at sub-micron resolution, via energy dispersive X-ray spectroscopy (EDX) [1]. In that regime, methods have been established to overcome potentially confounding influences. For instance, one can correct for X-ray absorption by extrapolation to very thin samples [2] or via the ζ-factor method [1]. Strong scattering from crystal planes can be avoided by selecting a "non-channeling" orientation.

Atomic resolution EDX analysis has recently become possible through improvements in scanning transmission electron microscopy (STEM) instrumentation [3,4]. However, it does not yet enjoy the quantitative success that makes it so powerful at lower resolutions. In particular, non-channeling conditions are seldom desirable at atomic resolution, on-axis conditions being needed for direct structure interpretation. Procedures for quantitative analysis and overcoming confounding influences like channeling in atomic resolution STEM EDX are just starting to be developed.

Kotula *et al*. suggest that atomic resolution STEM EDX images themselves be used as the basis for establishing the conversion factors needed for quantitative analysis by determining Cliff-Lorimer *k*-factors from the ratio of the mean signals from regions of known stoichiometry [4]. This is a promising approach, because mean STEM signals are known to be very robust, being independent of both coherent and incoherent lens aberrations [5]. However, though they have reduced sensitivity to channeling effects, they are not completely immune to them [5,6]. In particular, we show that under on-axis conditions, the Van Cappellen procedure of extrapolating to zero thickness [2] applied to the Kotula *et al*. approach for extracting *k*-factors from the experimental data [4] can often produce misleading results: the seemingly smooth trend from samples with thicknesses above ~100 Å may not be indicative of the true zero-thickness limit.

Figure 1 shows simulated STEM ADF and EDX data for $SrTiO_3$ for three different probe sizes. Below these images are plots of the ratios of the mean STEM EDX signals for select transitions. As per the discussion above, the trend evident in the Ti K / Sr K ratio for thicknesses above ~200 Å is different from that below it, and the trend evident in the O K / Sr K ratio for thicknesses above a mere ~80 Å is different from that below it.

The fact that the limitations imposed by channeling can be established through simulation suggests that simulation itself is a promising path to overcoming these limitations. Since *k*-factors must anyway be calibrated on a portion of specimen where the structure/composition is known, simulation can be used to model, and thereby correct for, the effects of channeling. When seeking to analyze new samples, channeling

is again a hindrance, and we argue that structure and composition determination will need to be performed simultaneously, with channeling-incorporating simulations underpinning the analysis.

References

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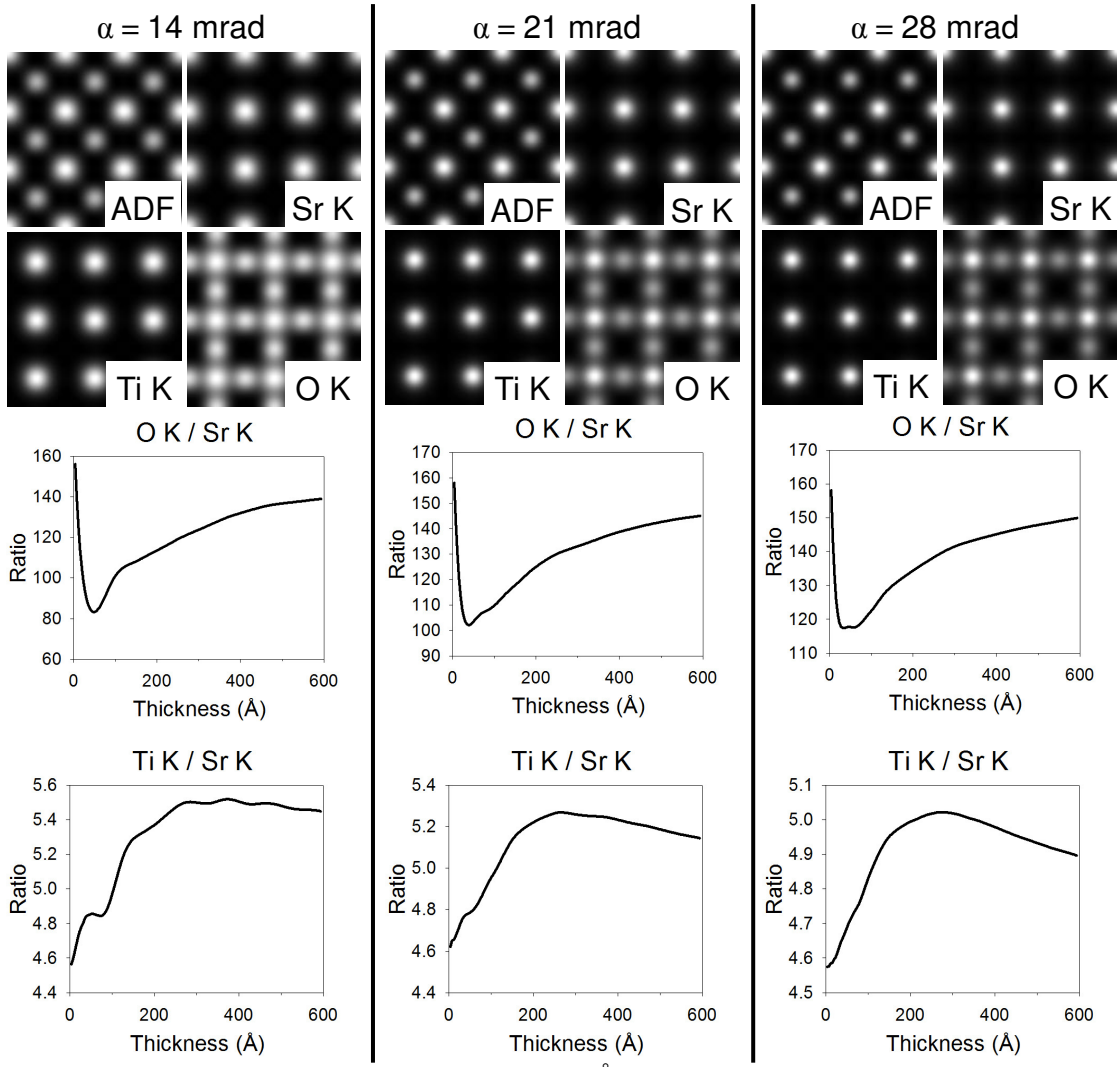

FIG. 1. STEM ADF and EDX simulations for a 300 Å thick specimen of $SrTiO_3$ viewed along the [001] orientation using 200 keV, aberration-free electron probes for the three different aperture sizes α listed. Below these are plots of select ratios of the mean STEM EDX signals as a function of specimen thickness. All simulations account for spatial incoherence via a Gaussian effective source of half-width-half-maximum 0.4 Å.