Energy dispersive X-ray analysis on an absolute scale in scanning transmission electron microscopy\textsuperscript{\ast,\ast\ast}

Z. Chen\textsuperscript{\ast,*}, A.J. D’Alfonso\textsuperscript{\ast,*}, M. Weyland\textsuperscript{\ast,d}, D.J. Taplin\textsuperscript{\ast}, L.J. Allen\textsuperscript{\ast}, S.D. Findlay\textsuperscript{\ast,**}

\textsuperscript{\ast}School of Physics and Astronomy, Monash University, Clayton, Victoria 3800, Australia
\textsuperscript{\ast}School of Physics, University of Melbourne, Parkville, Victoria 3010, Australia
\textsuperscript{d}Monash Centre for Electron Microscopy, Monash University, Clayton, Victoria 3800, Australia
\textsuperscript{\ast}Department of Materials Science and Engineering, Monash University, Clayton, Victoria 3800, Australia

Abstract

We demonstrate absolute scale agreement between the number of X-ray counts in energy dispersive X-ray spectroscopy using an atomic-scale coherent electron probe and first-principles simulations. Scan-averaged spectra were collected across a range of thicknesses with precisely determined and controlled microscope parameters. Ionization cross-sections were calculated using the quantum excitation of phonons model, incorporating dynamical (multiple) electron scattering which is seen to be important even for very thin specimens.

Keywords: scanning transmission electron microscopy (STEM), energy dispersive X-ray (EDX) spectroscopy.

1. Introduction

Analytical electron microscopy has long been able to determine elemental concentration ratios with a sensitivity of a few atomic percent in microanalyses via energy dispersive X-ray spectroscopy (EDX). This is done via EDX signal ratios and comparison with reference specimens to minimize the effect of uncertainties in factors such as thickness, ionization cross-section, fluorescence yield and detector geometry \cite{1, 2}. However, in principle, absolute-scale comparison with ionization cross-section calculations is possible. Recent developments in aberration-corrected electron optics and X-ray detector design \cite{3, 4} have facilitated scanning transmission electron microscopy (STEM) EDX mapping at atomic resolution \cite{5–12}, and on this length scale absolute elemental concentrations will often be more useful than relative concentrations. For instance, in nanoparticles, nanoprecipitates, or dopant segregation at interfaces, the absolute number of atoms of a given species contains critical information about their structural arrangement and distribution.

In this article, we show that absolute-scale agreement between experiment and simulations, which has recently been achieved in high-angle annular dark field (HAADF) imaging \cite{13–15} and electron energy loss spectroscopy \cite{16, 17}, is also possible in STEM EDX. We emphasize that, in on-axis conditions, quantitative agreement requires accounting for dynamical electron scattering, also called “channelling”, even for very thin specimens.

2. Absolute-scale EDX

EDX measurements were taken using an aberration-corrected FEI Titan\textsuperscript{\texttrademark} electron microscope operating at 302 kV. Experiments were carried out for a range of thicknesses in a SrTiO\textsubscript{3} crystal viewed along the [001] zone axis. The sample was prepared by cross-sectional tripod/wedge polishing, with final thinning by Ar-ion milling \cite{18}. Two different probe-forming aperture semi-angles were used, 15.2 and 21.5 mrad, both of which produce an atomically fine probe. However, the modest effective collection angle of the conventional Si(Li) detector (EDAX inc., nominal area 30 mm\textsuperscript{2}) used necessitated averaging the EDX signal over several unit cells to obtain good counting statistics. This forfeits atomic-resolution information but gains stability against noise and also substantially removes the deleterious effects of coherent and incoherent aberrations in the probe-forming optics \cite{19, 20}. Forfeiting atomic-resolution information is not a significant limitation for the present study. Up to the question of adequate signal-to-noise ratio, the scan-averaged spectra we obtain are equal to the mean signal of the atomic-resolution EDX image which could in principle be formed given the fine probe used – the reference HAADF images recorded during the experiment, an example of which is shown in Fig. 1(a), are atomic resolution images. It has been previously established that simulations and experiment are in excellent agreement as to the relative intensity distribution in atomic-resolution EDX (e.g. Ref. \cite{12}). Since, as we presently show, the factors needed to convert the simulations to an absolute number of measured X-ray counts are all multiplicative, de-
terminating all these factors would equally enable absolute-scale comparison of atomic-resolution EDX images.

Figure 1(b) shows a typical EDX spectrum averaged over the scan region shown in Fig. 1(a). The Ti K, Sr K and Sr L peaks are clearly visible. Figure 1(c-h) compares the experimental number of X-ray counts for the Ti K, Sr K and Sr L shells, for the two probe-forming apertures and a range of specimen thicknesses, all against simulations [21, 22] including channelling and against idealized “non-channelling” references. Non-channelling conditions are sought in lower resolution imaging to facilitate direct interpretation by orientating the sample such that atoms do not align into columns along the beam direction [23]. However, this is rarely desirable at atomic resolution since the atomic structure is clearly interpretable only when atomic columns are aligned along the beam direction. Two things are evident from Fig. 1. First, the absolute-scale quantitative agreement between the experiment and channelling simulation is excellent. Second, significant discrepancies occur between all these results and the non-channelling simulations even in the thinnest samples.

Measured X-ray counts and EDX simulations are put on the same scale using the following expression:

\[ N = I_{\text{inc}} T F_{\text{ion}}(t, X_{\text{abs}}) \omega \left( \frac{\Omega}{4\pi} \right) D_{\text{eff}}. \] (1)

We will discuss each factor in turn.

Number of X-ray counts, \( N \), for a particular peak:

The recorded spectra were background subtracted by fitting in the region between X-ray peaks following Huang [24]. The error bars were computed assuming Poisson statistics for both the X-ray peak and the background contributions.

Incident beam current, \( I_{\text{inc}} \):

The incident beam current was measured to be \( 2.31 \times 10^8 \) e/s for the 15.2 mrad probe-forming aperture and \( 4.68 \times 10^8 \) e/s for the 21.5 mrad aperture using the drift tube of a Gatan image filter.

Live dwell time, \( T \):

The live dwell time was 100 s. During this time, the probe was scanned over an area of uniform thickness encompassing several unit cells.

Fraction of incident electrons resulting in ionization plus a depth-dependent absorption correction, \( F_{\text{ion}}(t, X_{\text{abs}}) \):

The fraction of incident electrons resulting in ionization of the edge under consideration, incorporating both the ionization cross-section and how the electron probe scatters through the material, may be computed using [25–27]

\[ I(R, t) = \int_A \int_0^\infty |\psi(R, r_\perp, z)|^2 V_{\text{eff}}(r_\perp) X_{\text{abs}}(z) dz dr_\perp. \] (2)

where \( R \) denotes the probe-position on the surface, \( t \) the sample thickness, \( \psi \) the fast-electron wave function at a depth \( z \) in the crystal and \( V_{\text{eff}} \) the effective scattering potential for ionization. \( F_{\text{ion}}(t, X_{\text{abs}}) \) is the average of this quantity over probe position. Calculations were carried out using the quantum excitation of phonons model [21], as implemented in the software package μSTEM [22]. \( X_{\text{abs}}(z) \) is the fraction of generated X-rays that escape the specimen. As X-ray absorption by the specimen depends on the position at which the X-rays are generated, it is convenient to combine the depth integration over the ionization cross-section with the depth dependent absorptive term \( X_{\text{abs}}(z) = e^{-\mu(z)} \), where \( R(z) = z \cos(\alpha)/ \sin(\alpha + \theta) \) is the X-ray transmission path within the sample as illustrated in Fig. 2 for takeoff angle \( \theta \) and specimen tilt \( \alpha \), \( \mu \) is the mass absorption coefficient, values for which were taken from the tables in Ref. [28], and \( \rho \) is the density. The “thin-film criterion” asserts that in thin specimens X-ray absorption and subsequent fluorescence can be safely neglected. For the Sr K shell X-rays, \( X_{\text{abs}} \approx 1 \) at the thicknesses we consider. Absorption for the lower energy X-rays, i.e. the Ti K shell and Sr L shell, is potentially more significant, though for the thicknesses we consider the effect is still at the few percent level. Nevertheless, absorption has been included in all simulations in Fig. 1.

Fluorescence yield, \( \omega \):

The fluorescence yield is the fraction of ionization events which lead to emission of an X-ray. We use 0.0209 for the Ti K shell, 0.6745 for the Sr K shell [31], and 0.0256 for the Sr L shell [32].

Effective detector solid angle, \( \Omega \):

The effective detector solid angle in steradian (sr) incorporates such factors as the type of specimen holder and its tilt, the shape and active area of the detecting surface, and the distance between the sample and the detector [29]. This has been calculated following the approach of Zaluzec [29, 30] based on manufacturer provided specifications illustrated in the schematic in Fig. 2: distance to detector, \( d = 12.1 \) mm; detector active radius, \( r = 2.8 \) mm; detector tilt angle, \( \theta = 20.1^\circ \); and collimator obstruction fraction, \( f = 0.27 \) [33]. This results in \( \Omega = 0.11 \) sr, assuming no obstruction by the specimen holder. The holder used was an FEI low background (Be) double tilt holder. The information above implies a lower detector height (\( H_2 \)) of 1.36 mm, an upper detector height (\( H_1 \)) of 6.96 mm and a radial detector distance (\( D \)) of 11.3 mm. The side of the holder nearest the EDX detector has a half-width (\( \omega_r \)) of 3.21 mm and side wall half-height (\( h_s \)) of 0.59 mm [34]. We can therefore conclude that the tilt angles used – \( \alpha \) varied between 8.3° and 13.2° for different specimen areas – were well above the minimum holder tilt angle of 3.55° needed to avoid any holder penumbra.

Detector efficiency, \( D_{\text{eff}} \):

The detector efficiency includes the energy-dependent X-ray transmission through the detector window and its coatings, transmission through the front contact, the dead layer, and the absorption in the semiconducting detector crystal itself. The window is a MOXTEX AP3.3 polymer-based window with thin vertical silicon support bars. The support bars reduce \( D_{\text{eff}} \) by a factor of 0.383 [35]. For low X-ray energies (< 3 keV) this transmission is further reduced due to absorption by the polymer window itself. However, higher energy X-rays (> 9 keV) will transmit through the Si support bars, increasing transmission. A plot of the variation of transmission with X-ray energy has been supplied by the manufacturer [36]. Combining this transmission curve of the window with the 0.383 geometric
Figure 1: Absolute-scale comparison of experiment and simulation (with and without channelling) for different EDX edges and probe-forming aperture semi-angles: (a) HAADF image from one area; (b) EDX spectrum from the area in (a); (c) Ti K, 15.2 mrad; (d) Ti K, 21.5 mrad mrad; (e) Sr K, 15.2 mrad; (f) Sr K, 21.5 mrad; (g) Sr L, 15.2 mrad; and (h) Sr L 21.5 mrad.
Furthermore, as the L$_2$ levels of specimen mistilt and estimates of the aperture size. It is our experience that the L$_2$ age, which we take as our thickness estimates. We note that this metric has unambiguous and localized minima for each image (i.e. a sum square intensity difference). Therefore, Fig. 3(d) compares the PACBED thickness determination against that by quantitative HAADF [13–15] with the same aperture size as for STEM EDX. The total beam intensity for the different aperture sizes involved was carefully calibrated [39], and the experimentally-measured, two-dimensional detector response map was incorporated into the simulation [40]. The agreement between PACBED and quantitative HAADF thickness estimates are well within expected errors ($\leq 10$ Å) for the majority of points. The few exceptions may be due to areas of the specimen with a relatively larger amorphous layer.

4. Effects of channelling

In Fig. 1 the effect of channelling, not hitherto included in quantitative STEM EDX measurements [2], is clearly large, even though the position-averaged signal approach is believed to reduce the severity of channelling effects [20, 41]. From Eq. (2), neglecting X-ray absorption for simplicity, the probe-position averaged signal is given by

$$
\bar{I} \equiv \int_A I(R) dR = \int_A \int_0 \mathcal{P}(r, t) V_{\text{eff}}(r, t) dr dt,
$$

where

$$
\mathcal{P}(r, t) = \int_A \int_0 |\psi(R, r, z)|^2 dz dR
$$

gives the probability density of the fast electron projected across the specimen thickness and averaged over probe position. In the absence of channelling, this would be constant. However, as shown in Fig. 4(a) for a range of thicknesses and probe-forming semi-angles, this probability density peaks on the column sites. This is the source of the channelling enhancement: even averaged over probe position, the attraction of electrons to the atomic columns peaks the electron density in their vicinity (and correspondingly reduces it elsewhere, since conservation of electrons ensures that the total electron density in $\mathcal{P}(r, t)/t$ is constant). Moreover, this effect occurs even in very thin crystals.

The corresponding mean STEM EDX signals in Fig. 4(b) show that channelling is pronounced when the probe-forming aperture semi-angle is small but becomes weaker as the aperture semi-angle increases. This can be understood as follows. The STEM signal averaged over a unit cell is identical to the signal obtained by an incoherent set of plane waves with the same set of transverse momentum components as present in
the STEM probe [19, 20]. When the aperture is small, these plane waves are all close to the zone axis conditions and each channels strongly. As the probe-forming aperture semi-angle increases, an increasingly large fraction of the plane waves have high transverse momentum components and so more closely resemble non-channelling plane waves [42]. Figure 4 shows that a probe-forming aperture semi-angle of 50 mrad would greatly reduce, but not wholly eliminate, the channelling effect. A similar suppression of channelling has recently been demonstrated by tilting the specimen a few degrees off axis [12, 43].

As an aside, the equivalence noted above between unit-cell-averaged STEM signal and tilt-averaged incident plane waves means that the results we present could equally be obtained in a broad-beam illumination technique such as atom location by channelling enhanced microanalysis (ALCHEMI) [44, 45] by averaging over a suitable range of orientations. It would therefore be possible to perform the channelling simulations we described using ALCHEMI software (e.g. Ref. [46]) and interpret the results in that framework.

The Cliff-Lorimer k-factor commonly used in EDX quantification is defined as

\[ \frac{I_1}{I_2} = \frac{C_1}{C_2}, \]  

where \( I_1 \) and \( I_2 \) are measured EDX intensities and \( C_1 \) and \( C_2 \) denote concentrations (conventionally as a weight fraction) of species 1 and 2 [47]. The conventional definition assumes non-channelling conditions. It has recently been suggested that the ratios of mean intensities in atomic resolution EDX images might be used to approximate the Cliff-Lorimer k-factor [10]. The case of the Sr K / Ti K mean EDX intensity ratio is plotted in Fig. 4(c) as a function of thickness for various probe-forming convergence semiangles.

For smaller convergence angles, the k-factor has a strong nonlinear thickness dependence. We again see that a probe-forming aperture semi-angle of 50 mrad would greatly reduce the channelling effect: the mean EDX intensity ratio is almost constant with thickness. However, it does not wholly elimin-
Table 1: EDX intensity ratio of Sr K/Ti K. Thickness t → 0 gives the ratio for the non-channeling condition.

<table>
<thead>
<tr>
<th>Convergence angle</th>
<th>Thickness (A)</th>
<th>t→0</th>
<th>94</th>
<th>172</th>
<th>277</th>
<th>523</th>
</tr>
</thead>
<tbody>
<tr>
<td>15.2 mrad</td>
<td>Expt. Sim.</td>
<td>1.14</td>
<td>1.48(12)</td>
<td>1.41(08)</td>
<td>1.44(07)</td>
<td>1.41(05)</td>
</tr>
<tr>
<td>21.5 mrad</td>
<td>Expt. Sim.</td>
<td>1.14</td>
<td>1.24(07)</td>
<td>1.24(06)</td>
<td>1.33(05)</td>
<td>1.29(04)</td>
</tr>
</tbody>
</table>

References:


[34] Private communication from FEI company.


Figure 4: (a) Simulations of thickness projected, probe position averaged electron density divided by thickness (over 2 x 2 unit cells along the [001] zone axis of SrTiO$_3$). (b) Simulated Sr-K shell mean EDX intensity and (c) simulated Sr K / Ti K mean EDX intensity ratio as a function of thickness. Results are shown for a range of probe-forming aperture semi-angles.