Composition measurement in substitutionally disordered materials by atomic resolution energy dispersive X-ray spectroscopy in scanning transmission electron microscopy

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Abstract

The increasing use of energy dispersive X-ray spectroscopy in atomic resolution scanning transmission electron microscopy invites the question of whether its success in precision composition determination at lower magnifications can be replicated in the atomic resolution regime. In this paper, we explore, through simulation, the prospects for composition measurement via the model system of Al,Ga...As, discussing the approximations used in the modelling, the variability in the signal due to changes in configuration at constant composition, and the ability to distinguish between different compositions. Results are presented in such a way that the number of X-ray counts, and thus the expected variation due to counting statistics, can be gauged for a range of operating conditions.

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

1. Introduction

Analytical electron microscopy via energy dispersive X-ray spectroscopy (EDX) has proven to be a successful technique for exploring elemental composition in microanalysis, i.e. at sub-micron resolution. The equation relating the number of X-ray counts $N_A^{\text{peak}}$ in a given X-ray peak for element A to the weight concentration $C_A$ of that element is written in various forms in the literature, but following Zaluzec can be written as:

$$N_A^{\text{peak}} = \left[ \frac{c_A^{\text{peak}}(E_0)}{W_A} \omega_A \Gamma_A^{\text{peak}} \right] \cdot \left( C_A \frac{N_0 t \epsilon_t}{W_A} \right) \cdot \left( \frac{i T e_A^{\text{peak}} \Omega}{4 \pi} \right), \quad (1)$$

where $c_A^{\text{peak}}(E_0)$, $\omega_A$, and $\Gamma_A^{\text{peak}}$ denote the ionization cross-section for the shell in question at accelerating voltage $E_0$, the fluorescence yield, and the relative transition probability of the peak, $C_A$, $W_A$, $N_0$, $\rho$ and $\tau$ denote the weight concentration of element A, the atomic weight of element A, Avogadro’s number, the sample density and sample thickness; $i$, $T$, $\epsilon_t$ and $\Omega$ denote the current, the live time, the detector efficiency for the peak being measured and the detector solid angle. Converting the measured number of X-ray counts $N_A^{\text{peak}}$ to the sought weight concentration $C_A$ thus requires a large number of elemental properties [terms in the first bracket in Eq. (1)], sample geometry [terms in the second bracket in Eq. (1)], and instrumental properties [terms in third bracket in Eq. (1)] to be known. This can to some extent be sidestepped by examining ratios of the measured signals:

$$\frac{C_A}{C_B} = k_{AB}^{\text{peak}} \frac{N_A^{\text{peak}}}{N_B^{\text{peak}}}, \quad (2)$$

where $k_{AB}^{\text{peak}}$ is the Cliff-Lorimer k-factor [6]. The current, dwell time and detector solid angle genuinely drop out in taking this ratio, but most other factors are simply subsumed (including the instrument-dependent detector efficiency, which means the Cliff-Lorimer k-factor too is instrument dependent [3]). Nevertheless, the k-factors can be determined to a good degree of precision, either from first principles calculation of the cross-sections or from measurements on samples of known composition [1], with ~1% sensitivity possible for the latter [4].

There are various measures for the sensitivity limit in EDX. The minimum mass fraction – the smallest concentration of one element detectable in a matrix of another – was in 1980 in instruments capable of 20 nm spatial resolution estimated to be...
about 2 wt. %, well short of the precision possible in conventional electron microprobe analysis: higher resolution means a smaller interaction volume, and a correspondingly lower X-ray generation rate if the probe electron current density is similar [1]. In 2009 and using Eq. (1), Zaluzec [5] presented an analysis of the feasibility of single atom detection by EDX. Given the tiny interaction volume implied by a single atom, other factors must increase to give sufficient number of X-ray counts. Eq. (1) shows the most promising factors to be current, dwell time and detector solid angle. In the last decade or so, the large probe-forming convergence angles enabled by aberration-correction [7, 8] and the development of brighter electron sources [9] have significantly increased the incident electron counts. Eq. (1) shows the most promising factors to be current, dwell time and detector solid angle. In the last decade or so, the large probe-forming convergence angles enabled by aberration-correction [7, 8] and the development of brighter electron sources [9] have significantly increased the incident electron counts. Other factors must increase to give sufficient number of X-ray counts. Eq. (1) shows the most promising factors to be current, dwell time and detector solid angle. In the last decade or so, the large probe-forming convergence angles enabled by aberration-correction [7, 8] and the development of brighter electron sources [9] have significantly increased the incident electron counts. Given the tiny interaction volume implied by a single atom, other factors must increase to give sufficient number of X-ray counts. Eq. (1) shows the most promising factors to be current, dwell time and detector solid angle. In the last decade or so, the large probe-forming convergence angles enabled by aberration-correction [7, 8] and the development of brighter electron sources [9] have significantly increased the incident electron counts. Given the tiny interaction volume implied by a single atom, other factors must increase to give sufficient number of X-ray counts. Eq. (1) shows the most promising factors to be current, dwell time and detector solid angle. In the last decade or so, the large probe-forming convergence angles enabled by aberration-correction [7, 8] and the development of brighter electron sources [9] have significantly increased the incident electron counts. Given the tiny interaction volume implied by a single atom, other factors must increase to give sufficient number of X-ray counts. Eq. (1) shows the most promising factors to be current, dwell time and detector solid angle. In the last decade or so, the large probe-forming convergence angles enabled by aberration-correction [7, 8] and the development of brighter electron sources [9] have significantly increased the incident electron counts. Given the tiny interaction volume implied by a single atom, other factors must increase to give sufficient number of X-ray counts. Eq. (1) shows the most promising factors to be current, dwell time and detector solid angle. In the last decade or so, the large probe-forming convergence angles enabled by aberration-correction [7, 8] and the development of brighter electron sources [9] have significantly increased the incident electron counts. Given the tiny interaction volume implied by a single atom, other factors must increase to give sufficient number of X-ray counts. Eq. (1) shows the most promising factors to be current, dwell time and detector solid angle. In the last decade or so, the large probe-forming convergence angles enabled by aberration-correction [7, 8] and the development of brighter electron sources [9] have significantly increased the incident electron counts. Given the tiny interaction volume implied by a single atom, other factors must increase to give sufficient number of X-ray counts. Eq. (1) shows the most promising factors to be current, dwell time and detector solid angle. In the last decade or so, the large probe-forming convergence angles enabled by aberration-correction [7, 8] and the development of brighter electron sources [9] have significantly increased the incident electron counts. Given the tiny interaction volume implied by a single atom, other factors must increase to give sufficient number of X-ray counts. Eq. (1) shows the most promising factors to be current, dwell time and detector solid angle. In the last decade or so, the large probe-forming convergence angles enabled by aberration-correction [7, 8] and the development of brighter electron sources [9] have significantly increased the incident electron counts. Given the tiny interaction volume implied by a single atom, other factors must increase to give sufficient number of X-ray counts. Eq. (1) shows the most promising factors to be current, dwell time and detector solid angle.

The analysis of Zaluzec [5] implicitly assumed the single atom to be on the surface, or perhaps within a weakly scattering support. However, in many samples of interest, single atom impurities can be embedded within a crystalline matrix. In STEM annular dark field imaging, the effect of dynamical scattering of fine probes on on-axis crystals on the visibility of single atom substitutional dopants has been much explored [15–22]. Figure 1(a) shows that, unsurprisingly, the same considerations apply for the EDX signal of a single Al atom substitutionally present along a Ga column in GaAs viewed along the [110] zone axis. Figure 1(b) helps clarify how this comes about: the probe electron density scattering along the Ga column is not uniform, but instead shows oscillatory behaviour, a process referred to loosely as “channelling.” (The difference in shape between Figs. 1(a) and 1(b) mainly results from the for-}

![Figure 1](image-url)

**Figure 1:** (a) Depth dependence of the EDX signal of a single Al atom in a Ga column in GaAs viewed along the [110] axis. (b) Integrated probe intensity within a disk of radius 0.3 Å around a Ga column as a function of the depth into the crystal for the probe centred on the Ga column.

Channelling has implications for interpretation of atomic resolution STEM EDX data. Kotula et al. [23] find k-factor style analysis at atomic resolution in a Y2Ti2O7 pyrochlore is limited by the presence of a “background” signal that arises from probe scattering and spreading. Forbes et al. [24] show that, despite having the same oxygen concentration, the oxygen EDX signal on the TiO and pure O columns in SrTiO3 differs due to the difference in scattering along these two distinct columns. Kohleitner et al. [25] extend this to the relative distribution of signals from all elements in 2D STEM EDX images of SrTiO3. Neglect of these effects for quantification in thin samples seems to show a degree of success [26–28], perhaps because integrating about columns reduces the severity of channelling effects [24, 30], which can become significant in samples only a few nanometers thick [31]. These complications significantly hamper the application of the k-factor approach to atomic resolution STEM EDX data.

To include channelling, Eq. (1) can be generalized – in a notational compromise between Ref. [5] and Refs. [31, 32] – to

$$N_A^\text{peak} \left( \mathbf{R}, \Delta f, t \right) = F_A^\text{peak} \left( \mathbf{R}, \Delta f, t \right) \omega_A^\text{peak} \left( \Omega_{4\pi} \right), \quad (3)$$

where R denotes the position and Δf the defocus of the STEM probe, and $F_A^\text{peak} \left( \mathbf{R}, \Delta f, t \right)$ gives the fraction of incident electrons causing ionization events of element A potentially leading to the emission of X-rays for the peak in question. Means for calculating $F_A^\text{peak} \left( \mathbf{R}, \Delta f, t \right)$ are well-established [33, 35] and will be discussed in greater detail in section 4. Using such simulations and a carefully characterized experiment – for which detector characterization is particularly important [36–38] – Chen et al. have shown good agreement between simulated and experimental STEM EDX signals on an absolute-scale using an atomically fine electron probe [31, 32]. That work was proof-of-principle, using the well-known SrTiO3 structure. In absolute-scale quantitative high angle annular dark field imaging, the first proof-of-principle experiments [39, 40] were followed up with applications, most notably the determination of composition in semiconductor materials by Rosenauer and co-workers [41, 45].
This paper considers the prospects for and precision with which composition in substitutionally disordered materials can be determined by quantitative STEM EDX imaging at atomic resolution in on-axis conditions. In principle, by its elemental specificity EDX should be more suited to this problem than high angle annular dark field imaging. However, it is similarly sensitive to channelling effects and has a much lower signal to noise ratio, both limiting the precision with which different compositions can be distinguished. Figure 2 sketches the first issue. Figure 2(a) shows one slice through an Al\textsubscript{0.2}Ga\textsubscript{0.8}As model structure in which Al atoms (orange, smaller) are substitutionally doped into Ga sites in the Ga atom (green, larger) columns and the [110] zone axis is down the page. Since the doping level is 20\%, the expected number of dopants in a ten atom column is two. Three columns in our model structure contain exactly two dopants, but, because the doping is assumed to be random, two columns have only one dopant and another two have three. This is reflected in the STEM EDX map in Fig. 2(b) and the line profile in Fig. 2(c), simulated using the quantum excitation of phonons model [46] further discussed in Section 3. Specifically, columns with fewer dopants tend to have lower intensity than columns with more dopants, a positive sign as it suggests that composition might be distinguishable on a column-by-column basis. However, closer inspection reveals that columns with the same number of dopants can have significantly different intensities depending on the configurational distribution of these dopants in depth. This is perfectly consistent with the behaviour seen for the single dopant in Fig. 2(a), but adds a degree of uncertainty about whether STEM EDX signal variations represent a change in composition (which we will take to mean fraction of dopants in a column) or a change in configuration (which we will take to mean the ordering of dopants along a column). Another possibility – which is present in Fig. 2(b) but because of the thin sample is only a small effect there – is that two columns of similar composition and depth configuration could have different intensities because their neighbouring columns have different composition, which contributes as the probe spreads via channelling and thus quantitative imaging [42, 43, 45, 51], may be tolerably neglected. Experimental studies on similar systems include GaAs/AlGaAs core shell nanowires [50] and AlAs/GaAs interfaces [52, 53]. The [110] axis in zinc blende structures is also known to be a fairly strong channelling condition [49].

All simulations presented assume 300 keV electrons. Two different probe-forming apertures will be considered. The first, $\alpha = 18.4$ mrad, has been chosen as giving optimal coupling to the so-called column s-state of a pure Ga column in GaAs viewed along the [110] orientation [54]. The other, $\alpha = 30$…

Figure 2: (a) Schematic of the configuration of substitutionally doped Al atoms (orange, smaller) along Ga atom (green, larger) columns in Al\textsubscript{0.2}Ga\textsubscript{0.8}As with the [110] zone axis down the page. Also shown are the STEM EDX (b) image and (c) line scan across the set of columns in (a). The numbers below the image in (b) indicate the number of Al atoms in the column.
mrad, is taken as an example of a notably larger probe-forming angle, a circumstance which reduces depth of focus \[55\,\text{and should reduce (though will not eliminate)}\] channelling effects \[31\,\text{and 57}.\] For both probes, spatial incoherence is incorporated through a Gaussian incoherent effective source distribution with half-width-half-maximum 0.8 Å.

Using Eq. 1 – taking a fluorescence yield of 0.03872 for the Al K peak (Table 8 in Ref. \[58\]) and the detector efficiency \(\varepsilon_{\text{peak}}^2\) to be unity – all simulated STEM EDX signals will be given in units of X-ray counts per nanoampere per steradian per second. These simulations represent the ideal, “infinite dose” result. However, these units allow the reader to factor back in current, detector collection angle and dwell time to determine the expected number of X-ray counts under such assumptions. Shot noise being a Poisson process, the mean error is then the square root of the number of counts.

3. Comparison of approximations for simulations

The fraction of incident electrons causing ionization events in Eq. 1, \(F(R, \Delta f, t)\), is well-described by the overlap between the probe electron density and an effective scattering potential \[33\]:

\[
F(R, \Delta f, t) = \int_{0}^{\pi} \int_{0}^{2\pi} \int_{-\infty}^{\infty} \phi(r_{\perp}, z, R, \Delta f) \psi_{\text{eff}}(r_{\perp}, z) dr_{\perp} dz ,
\]

where \(\phi(r_{\perp}, z, R, \Delta f)\) denotes the wavefield of the probe electrons within the sample as a function of spatial coordinates \(r_{\perp}\) in the plane perpendicular to the optical axis and \(z\) along the optical axis, and \(\psi_{\text{eff}}(r_{\perp}, z)\) is the effective scattering potential for ionization \[33\,\text{and 55, 60, 61}\]. Though not strictly \(\delta\)-function like, \(\psi_{\text{eff}}(r_{\perp}, z)\) is highly localized upon atomic sites \[62\] and is essentially a property of the sample, though it does depend on accelerating voltage. By contrast, the probe electron density within the sample depends on both the incident probe geometry and the detailed, possibly-multiple elastic and inelastic scattering of the fast electrons through the sample. In this section we compare four different approximations for calculating the probe electron density, shown schematically in Fig. 3 which lie on a continuum of trading off quantitative rigour against conceptual and analytic simplicity. Figure 3 further shows Al K-peak STEM EDX simulations from an Al$_{0.5}$Ga$_{0.5}$As sample in [110] zone axis orientation for a range of thicknesses. For each thickness and model, Fig. 3 shows a STEM EDX image and plot of the STEM EDX signal, integrated over a disk of radius 1 Å about each column (drawn from a set of five such images, only one of which is shown) and grouped by the number of Al atoms in the column.

The quantum excitation of phonons (QEP) model \[43\], or the operationally-equivalent-but-conceptually-semi-classical frozen phonon model \[63\,\text{and 64}\], Fig. 3(a), is our most rigorous model, accounting for full multiple elastic and, to a good approximation, thermal scattering of the probe electron density by the specimen. Because thermally scattered electrons are incoherent relative to elastically scattered electrons \[65\], the probe electron density cannot strictly be written as the mod-square of a single wavefunction \[3\] and so Eq. 4 can more generally be written as

\[
F(R, \Delta f, t) = \int_{0}^{\pi} \int_{0}^{2\pi} \int_{-\infty}^{\infty} \rho(r_{\perp}, z, R, \Delta f) \psi_{\text{eff}}(r_{\perp}, z) dr_{\perp} dz ,
\]

where \(\rho(r_{\perp}, z, R, \Delta f)\) denotes the total probe electron density within the sample. That said, the total signal can be decomposed into a sum of the contributions from the elastically scattered electrons and the thermally scattered electrons \[46\,\text{and 66}\], offering some insight into the form of the EDX signal \[24\]. The price of this quantitative rigour is that the calculations can be time consuming, although the increased use of GPU-based or otherwise parallelized code \[67\,\text{and 70}\] ameliorates this somewhat.

The absorptive model, Fig. 3(b), accounts for full multiple elastic scattering of the probe electron density by the specimen, but handles inelastic scattering by “absorption”, removing those electrons which have undergone inelastic scattering from the electron density. Inelastic scattering is taken to include thermal diffuse scattering as it involves a change in the quantum state of the specimen, even though the energy loss is very small \[65\]. Comparing Figs. 3(a) and (b), the 2D STEM EDX maps for the QEP model and absorptive model are seen to be very similar. Only in the quantitative signals do we see that the signal strength in the QEP model starts to exceed that in the absorptive model for sample thicknesses beyond about 100 Å. This behaviour, previously explored in quantitative high angle annular dark field imaging \[39\], arises because those electrons which undergo thermal scattering – an increasingly large fraction of the total electron density with increasing sample thickness – do not, as the absorptive model assumes, disappear but are still scattering through the sample and still capable of causing ionization events which may lead to X-ray emission. Thus by not modelling the contribution due to electrons after they have been thermally scattered, the absorptive model reduces computational complexity at the expense of also reducing accuracy.

The 3D linear approximation \[71\], Fig. 3(c), neglects both inelastic and elastic scattering of all probe electrons by the specimen. Eq. 4 then simplifies to

\[
F(R, \Delta f, t) = \int_{0}^{\pi} \int_{0}^{2\pi} \int_{-\infty}^{\infty} \left|\psi_{0}(r_{\perp} - R, z - \Delta f)\right|^{2} \psi_{\text{eff}}(r_{\perp}, z) dr_{\perp} dz
\]

where \(\psi_{0}\) denotes the elastic wavefield in free-space and \(\otimes\) denotes convolution \[6\]. As shown in Fig. 3(c), this model still

\[\text{Note: the minus signs introduced in the final step are necessary because of the inversion implied by the formal convolution definition. For rotationally symmetric probes, they may be dropped.}\]

\[\text{5It can be expressed as the average over mod-squares of a series of inelastic wavefunctions (QEP model), or, to a good approximation, as per the frozen phonon formulation, as the average over mod-squares of elastic wavefunctions from different configurations.}\]
Figure 3: This figure compares (a) the quantum excitation of phonons / frozen phonon model, (b) the absorptive model, (c) the 3D linear approximation and (d) the object function approximation. Conceptual schematics of the probe evolution in the different models are shown on the left, where the green shading indicates elastically scattered electrons and orange shading indicates thermally scattered electrons. On the right, simulated Al K-peak STEM EDX images are shown for five different thicknesses, accompanied by a plot of the integrated intensity within a disk of radius 1 Å about the columns (from the image shown and four others with different configurations not shown) as a function of the number of Al atoms in the column. For each thickness, the STEM images for different models use the same structure and are shown on the same contrast scale. Different random Al/Ga distributions were generated for the different thicknesses, so no similarity is expected in the appearance of images from different thicknesses.
predicts signal variation with both the number and the configuration of atoms along the column, as evident in the plots which show, for columns with the same number of dopants, an increasing spread of counts with increasing sample thickness. However, the geometric probe spreading leads to rapid diffusion of the probe electron density, evident for thicker samples in the lower signal and contrast than in the QEP and absorptive models. That said, the 3D linear approximation is the basis for depth sectioning, determining 3D structure by recording images at different defocus values. Neglecting scattering of the probe by the sample has been shown to suffice for amorphous specimens of light elements.

The object function approximation assumes that the probe electron density inside the crystal remains identical to its form on the surface: \( \psi(r_{\perp}, z, R, \Delta f) \equiv \psi_0(r_{\perp} - R, -\Delta f) \), thereby eliminating any depth dependence from the probe electron density. Eq. (4) then simplifies to

\[
F(R, \Delta f, t) = \int |\psi_0(r_{\perp} - R, -\Delta f)|^2 \int |V_{\text{eff}}(r_{\perp}, z)| dz \, dr_{\perp}
\]

\[
= |\psi_0(-R, -\Delta f)|^2 \otimes_{\bf R} V_{\text{eff}}(R),
\]

in which \( V_{\text{eff}} \) denotes the depth-averaged effective scattering potential. This model explains the qualitative appearance of atomic resolution STEM images with peaks at column locations of shape and extent primarily determined by the probe intensity. It implies that, to the limits imposed by bandwidth limiting and noise, the probe intensity distribution can be deconvolved from the experimental image. As the simulated Al K-peak STEM EDX maps and plots of integrated signal about the Al-containing columns in Fig. 3(d) show, this model predicts that all configurations of atoms along a column with the same composition will give the same STEM EDX intensity, which is seen not to be true even in the 20 Å thick case in the more rigorous QEP and absorptive models.

The simpler models do capture some aspects of the physics. The background level (signal between columns) in the QEP and absorptive models is seen to be similar to that in the 3D linear approximation, evidence that geometric probe spreading is a reasonable first-order approximation to the scattering evolution of a probe placed between columns. Conversely, the on-column signal strength in the QEP and absorptive models is seen to be similar to that in the object function approximation, evidence that much of the electron probe does indeed “channel” along the column.

Table 1 shows a statistical analysis of the Al K-peak STEM EDX signals from that subset of columns with exactly 50% Al occupancy for different dopant configurations and different doping environment. The simulations in Fig. 3 and the statistical results in Table 1 support the expectation that all the models give the same result in the limit of very thin crystals, where scattering and spreading of the fast electrons is yet to appreciably alter the probe electron density. However, the shortcomings of the object function approximation and the 3D linear approximation for quantitative work are already apparent in thin crystals: Table 1 shows the error to be around 15% by 20 Å and 25% by 40 Å. These simulations further show the absorptive model to be quantitatively reliable (error below 5%) to about 100 Å and qualitatively reasonable beyond that. Because absorptive model calculations are faster than QEP models, it may be convenient for qualitative work. However, for quantitative work in all but the thinnest of samples, the QEP model is the most reliable of those models considered.

One common model not considered in detail here (but touched on in section 3) is the fractional occupancy approach, also called partial occupation, which handles a mixture of elements via a similar mixture of scattering potentials on each site. (Note: some care is needed to implement this in the frozen phonon model.) It can better include channelling than either the object function or 3D linear approximations, but in its standard form predicts results independent of configuration along a column. One possible modification is to calculate the probe electron density \( \rho(r_{\perp}, z, R, \Delta f) \) via the QEP model based on a fractional occupancy structure but use this density in Eq. (5) together with effective scattering potentials \( V_{\text{eff}}(r_{\perp}, z) \) which correctly account for configuration. Our experience (results not shown) is that it gets the scale and spread of the signals from different configurations about right, but can differ appreciably from the full QEP results for any individual configuration. Very recently, van den Bos et al. presented an atomic lensing model which is shown to handle mixtures in high angle annular dark field simulations for a very efficient set of calculations. If valid for STEM EDX – which seems likely but needs testing – this may be an efficient alternative. Note, though, that the atomic lensing model does not include the cross-talk effect.

### 4. Quantification in a substitutionally disordered structure

The discussion of Fig. 3 in the previous section focused on the comparison between the models. In this section we use the most rigorous model – the QEP / frozen phonon model – and explore the implications of its predictions for STEM EDX imaging of substitutionally disordered materials.

Fig. 4(a) reproduces the plot from Fig. 3(a) of integrated column Al K-peak STEM EDX signals from Al\(_{0.5}\)Ga\(_{0.5}\)As viewed along the [110] zone axis as a function of the number of Al atoms in the column for a 160 Å thick sample. The average Al K-peak EDX signal increases with the number of Al atoms in the column. The spread in signal from columns with the same composition but different depth configurations of Al atoms is appreciable. While only a subset of the very large number of possible configurations has been explored, the distributions (most with over twenty different configurations) seem representative. The difference in average number of counts/nA/sr is between successive numbers of dopants is about 60, but the standard deviation in spread for a fixed number of dopants is also about 60. Consequently, on a column-by-column basis for this 160 Å thick sample it would typically be difficult to distinguish configuration variability from genuine differences in composition of ±2 atoms in a 3σ confidence level. The uncertainty will be worse if a stricter 2σ or 3σ confidence level is used. For thicker samples, for example 320 Å shown in Fig. 3(a), the uncertainty will be still worse.
Note that the variation seen in Fig. 4 is due to difference in configuration and not to shot noise, since these simulations are effectively infinite dose results. It may well be, however, that shot noise is at least as limiting, if not more so. Consider the case of 20 dopants in Fig. 4(a), which gives an average number of counts/nA/sr/s of 1317. For a typical current of 0.1 nA, a multiple detector system with total solid angle 0.5 sr, and a column dwell time of 0.4 s (8 ms per pixel after scan averaging and four probe points per 1 Å linear scan), the total number of X-ray counts would be 26, giving a shot noise standard deviation of around 20%, four times as large as the configurational standard deviation of around 5%, as shown in Table 1. Obtaining precision limited by the configurational variation may thus only be possible in samples which will withstand high currents and/or a large degree of scan averaging. Novel configurations which increase the detector solid angle would help too.

Table 1: Statistical analysis of Al K-peak STEM EDX signal from that subset of columns with exactly 50% Al occupancy in Ga$_{0.5}$Al$_{0.5}$As. The error is the percentage difference of the different approximations relative to the QEP simulation. The mean and standard deviation (St. dev.) are given in units of counts/nA/sr/s.

<table>
<thead>
<tr>
<th>Thickness (Å)</th>
<th>QEP Mean</th>
<th>St. dev.</th>
<th>Absorptive Mean</th>
<th>St. dev.</th>
<th>Error Mean</th>
<th>St. dev.</th>
<th>Error Mean</th>
<th>St. dev.</th>
<th>Object function</th>
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<td>191</td>
<td>10</td>
<td>187</td>
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<td>1</td>
<td>-14%</td>
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<td>1</td>
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<td>18</td>
<td>363</td>
<td>16</td>
<td>-3.6%</td>
<td>268</td>
<td>-29%</td>
<td>277</td>
<td>1</td>
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<tr>
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<td>-35%</td>
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<tr>
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<td>1317</td>
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<td>1225</td>
<td>67</td>
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<td>2253</td>
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<td>1370</td>
<td>-39%</td>
<td>2217</td>
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Table 2: Statistical analysis of Al K-peak STEM EDX signal from that subset of columns with exactly 50% Al occupancy in Ga$_{0.5}$Al$_{0.5}$As. The error is taken to be the standard deviation divided by the mean, expressed as a percentage. The mean and standard deviation are given in units of counts/nA/sr/s. The focal average is obtained by averaging different probe focus maps from 0 to −160 Å with a 40 Å interval.

<table>
<thead>
<tr>
<th>α = 18.4 mrad</th>
<th>α = 30 mrad</th>
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<tr>
<td>Δf = 0</td>
<td>Δf average</td>
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<tr>
<td>Mean</td>
<td>1317</td>
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<tr>
<td>St. dev.</td>
<td>63.6</td>
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<tr>
<td>Error</td>
<td>4.8%</td>
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</table>

Figure 4: Averaged column Al K-peak STEM EDX signals from a 160 Å thick sample of Al$_{0.5}$Ga$_{0.5}$As viewed along the [110] zone axis plotted as a function of the number of Al atoms in the column. Results are shown for an 18.4 mrad (a,b) and 30 mrad (c,d) probe-forming aperture semiangle, and for a fixed defocus on the sample entrance surface (a,c) and for an average over defocus values from entrance to exit surface (b,d).
Supposing, though, that the experiment can be carried out in such a way that counting statistics are not the limiting effect, it is worth considering what may be done to reduce the configurational variation. Since it is a consequence of channelling, one option is to change the degree of channelling by changing the probe-forming aperture angle, since in periodic samples it is known that the probe-position averaging over a unit cell for larger probe-forming semiangle reduces the effects of channelling [31]. Results for a 30 mrad probe-forming aperture angle are shown in Fig. 4(c). Contrary to our objective, it is seen that this has increased the variability due to configurations while reducing the average number of counts, a consequence of the greater probe spreading and cross-talk effect. Another approach is to average over defocus, since in a geometric optics picture this might be expected to give a more uniform weighting of contributions from different depths [80]. Simulations averaging over defocus from 0 Å (entrance surface) to ~160 Å (underfocus equal to the specimen thickness) with a 40 Å increment are shown in Fig. 4(b) for the 18.4 mrad probe-forming aperture semiangle and Fig. 4(d) for the 30 mrad probe-forming aperture semiangle. In both cases, defocus averaging is indeed seen to notably reduce the configurational variation in the signal, potentially improving the precision to ±1 atom. Table 2 quantifies these tendencies by showing a statistical summary for the case of 20 Al dopants.

The analysis of Fig. 4 takes advantage of the controlled input to the simulations: the number of dopants in each column is known. In real experiments this will not be the case. Fig. 5 looks at the distribution in integrated column intensities for many columns (specifically 240: five model structures each with 48 distinct columns) comparing a sample of composition Al$_{0.5}$Ga$_{0.5}$As, i.e. 50% Al doping, with one of Al$_{0.45}$Ga$_{0.55}$As, i.e. 45% Al doping. A 160 Å thick sample (i.e. 40 atoms along each column) is again considered, and results shown for (a) the 18.4 mrad probe-forming aperture semiangle, and for the 30 mrad probe-forming aperture semiangle for (b) the probe focused on the entrance surface and (c) defocus averaged over sample thickness. A statistical summary of the mean and standard deviation of these distributions is given in Table 3. The degree of overlap between the two distributions is very similar in all cases. This occurs because despite the greater precision with which the number of dopants in any individual column can be determined in the defocus average case, Fig. 4(d), under the assumption of random substitutional disorder the number of dopant atoms varies from column to column. For a random distribution of dopants, the number of dopants in a column follows a binomial distribution, which in the present 50% doping in a 160 Å specimen implies a standard deviation of three atoms. Thus in Fig. 5(c), we would be more confident that a column with 1000 counts/nA/sr/s contains 21 or 22 Al dopants than we would in Fig. 5(b), but in both cases we could only assess the nominal average composition by averaging over several columns. That said, because the fractional difference in mean intensities between the 45% and 50% Al composition cases is essentially the same for all conditions in Fig. 5 for estimating the average composition there is no appreciable advantage in the more complex conditions of larger probe-forming apertures or defocus averaging: all contain a similar uncertainty as that intrinsically present in the dopant distribution.

It follows therefore that distinguishing phases of different compositions cannot be done on a column-by-column basis, but only by distinguishing the distribution of column intensities.
ties over two different regions, which may require an EDX map from a relative large area of a specimen, say hundreds of atomic columns, to achieve good statistics. In Fig. 5 the dashed lines show Gaussian functions with peak position and width set to the mean and standard deviation of the column EDX signal distribution for the two different compositions. The Gaussian is seen to be a good fit. Moreover, Table 3 shows the mean signal to be well estimated by a fractional occupancy simulation, which would allow a fast estimation of the expected mean for a given composition. Going further, since a random distribution in a phase of uniform composition implies a binomial distribution of atoms in the different columns, and thus an approximately binomial distribution of column EDX signals (which, Fig. 5 shows, can be reasonably approximated by a Gaussian distribution), plotting the histogram of all the atomic column EDX signals and checking whether it can be fitted by single or multiple Gaussian functions could be used to determine whether or not there is a single compositional phase. Deviations from the expected distribution might also imply a deviation from random distribution of dopants. Note that the distributions in Fig. 5 assume infinite dose – in practice the distributions will be broadened by shot noise.

5. Conclusion

In summary, distinguishing different compositions in STEM EDX remains a challenging prospect at atomic resolution. One reason is that channelling means that the variation in signal from different configurational distributions can be comparable to a significant compositional variation for all but the thinnest of samples. For composition assessment on a column-by-column basis, defocus averaging is predicted to reduce the sensitivity to configurational distribution somewhat. Another reason is that obtaining sufficient X-ray counting statistics is very challenging.

For a given model system, absolute scale simulations enable us to predict in advance the expected number of X-ray counts and thus whether the signal of interest should be reliably detectable. This enables decisions to be made about the minimum required dose. The present results suggest, though, that extending the success of STEM EDX for precision elemental composition determination in microanalysis to the atomic resolution regime will require further improvements in detector collection angle and stability for multiple scan averaging.

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