Elemental mapping in scanning transmission electron microscopy

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Abstract. We discuss atomic resolution chemical mapping in scanning transmission electron microscopy (STEM) based on core-loss electron energy loss spectroscopy (EELS) and also on energy dispersive X-ray (EDX) imaging. Chemical mapping using EELS can yield counter-intuitive results which, however, can be understood using first principles calculations. Experimental chemical maps based on EDX bear out the thesis that such maps are always likely to be directly interpretable. This can be explained in terms of the local nature of the effective optical potential for ionization under those imaging conditions. This is followed by an excursion into the complementary technique of elemental mapping using energy-filtered transmission electron microscopy (EFTEM) in a conventional transmission electron microscope. We will then consider the widely used technique of Z-contrast or high-angle annular dark field (HAADF) imaging, where it has recently been shown that intensity variations can be placed on an absolute scale by normalizing the measured intensities to the incident beam. Results, showing excellent agreement between theory and experiment to within a few percent, are shown for Z-contrast imaging from a sample of PbWO₄.

1. Introduction
Using scanning transmission electron microscopy (STEM) 2D atomic resolution chemical mapping in a specimen can be obtained using electron energy loss spectroscopy (EELS) [1-3] and, more recently, energy-dispersive X-ray (EDX) analysis [4]. We will show that this is also possible in energy-filtered transmission electron microscopy (EFTEM), though more care needs to be taken to ensure that atomic resolution information is present and simulations may be needed to decode the atomic resolution information in the data [5]. Z-contrast imaging also allows for some degree of quantitative elemental mapping through the strong atomic number dependence of the signal. A complete understanding of such images requires detailed quantitative comparisons between simulations and experiments, which has only recently become possible [6,7].
2. Chemical mapping using EELS

Since atomic resolution EELS was first demonstrated in the early 1990’s using STEM [8-10], there has been rapid progress. Aberration correction in the electron optics has allowed probe sizes of less than 0.1 nm and this, combined with increases in EELS detector efficiency, has allowed chemical mapping of crystals in two dimensions [1-3]. Such maps are not always directly interpretable [1,11]. The nonlocality of the interaction is expected to reduce with increasing detector collection angle (see, for instance, Ref. [3], which uses a detector angle as large as 60 mrad on a Nion UltraSTEM system). However, elastic scattering effects may still hamper simple image interpretation. This can be seen in figure 1. The O signal in <111> Bi$_{0.5}$Sr$_{0.5}$MnO$_3$ shown in (a) is consistent with the placement of those atoms, albeit rather delocalized. However the Mn signal in (b) is a minimum on the Mn columns.

Simulation shows that this unexpected result arises because the probe placed between the columns interacts significantly with the delocalized transition potential and this yields more signal than that when the probe is placed on column, where thermal diffuse scattering depletes the probe. Using a system with an even larger detector angle, Wang et al. [11] obtained a contrast reversal when images were constructed from differing regions of the energy loss spectra, as shown in figure 2. This case is particularly interesting: the elastic scattering is common to both images, so the differences are purely due to the transition potentials at the lower energy loss window being more delocalized, reaching further into the open channels between the Si dumbbells.

![Figure 1. Experiments and simulations of Bi$_{0.5}$Sr$_{0.5}$MnO$_3$ oriented along the <111> zone axis. (a) O K edge and (b) Mn L$_{2,3}$ edge STEM EELS images. The EELS maps were generated by integrating over a 30 eV window above the respective ionization thresholds (shown in grey shading on the spectra to the right, which are summations of all the spectra in the adjacent EELS maps). The simulations assume a 40 nm thick sample.](image1)

![Figure 2. Comparison between experimental and simulated images of <011> Si. (a) 143–163 eV energy filtered EELS, and (b) 280–300 eV energy filtered EELS images. (c) A typical acquired Si EELS spectrum showing the background fit curve subtraction. All images were acquired simultaneously.](image2)
3. Chemical mapping using EDX

One advantage that STEM EDX has over STEM EELS is that the inelastic interaction is effectively local, like that in high angle annular dark field (HAADF). This is because all ionization dynamics are sampled: EDX is effectively equivalent to STEM EELS with a detector that covers the whole solid angle. The effective large detector averages over the phase information and leads to incoherent imaging [12,13] and the resulting image can usually be directly interpreted. The effective local scattering potentials for Ti K-shell x-ray emission and the sum of the Sr K- and L-shell potentials for x-ray emission along the <110> direction in <001> SrTiO$_3$ are compared to that for HAADF in figure 3 and exhibit a similar localization. In figure 4 we show line scans for a test sample of <001> SrTiO$_3$ based on STEM EDX and using an FEI Titan 80-300 operating at 300 keV [4]. The sample thickness was estimated to be 100 nm (a specimen of this thickness was needed to ensure sufficient x-ray counting statistics). As the probe was not aberration corrected, the probe forming aperture semi-angle was limited to 9.6 mrad and the probe was under-focused by 56 nm into the specimen. The EDX detector subtended a collection angle of 0.13 sr. Theoretical simulations are in good agreement with the experimental data [4].

Following the formulation outlined in Ref. [14], simulations confirming the data were performed using a hybrid of the frozen phonon (FPh) algorithm to account for thermal scattering [15] and the mixed dynamical form factor (MDFF) [16] to model ionization. The assumption is made that the total cross section for all x-ray emission events corresponding to filling a hole in the K- or L-shell is proportional to the total cross section for K- or L-shell ionization respectively.

![Figure 3. The effective scattering potential for HAADF for a detector spanning 60-160 mrad (black), Ti K-shell x-ray emission (red) and the sum of the Sr K- and L-shell potentials for x-ray emission (blue) for EDX. The scattering potential is for the <110> direction for a single unit cell of SrTiO$_3$. The Sr and Ti sites are indicated by the blue and red circles respectively. Each line plot has its maximum value normalized to one.](image)

![Figure 4. (a) Reference HAADF line scan image of the SrTiO$_3$ sample along <110>. (b) EDX line scans for Ti (red, below) and Sr (blue, above). The maxima in the EDX line scans correlate with the expected atomic positions.](image)
4. Atomic resolution EFTEM
EFTEM based on inner-shell ionization can contain atomic resolution information [5]. EFTEM has the advantage that the spatial information needed for elemental mapping is acquired in parallel, allowing for precision measurements of column locations. Experimental data taken on a 6 nm thick specimen of LaB₆ viewed down the [001] zone axis and monitoring the lanthanum N₄,₅ edge are shown compared to a first principles calculation in figure 5. Calculations show that the transition potentials in the vicinity of the N₄,₅ edge of La (threshold energy 99 eV) are such that an EFTEM image of a suitably thick specimen of LaB₆ contains information on the location of the La columns. The simulation confirms that the brightest points in the image correspond to the positions of the La atoms. Previous work makes such a direct interpretation somewhat surprising [17,18], though the specimen is quite thin. The localization of the transition potentials is such that elastic contrast is only weakly preserved in the EFTEM image and the degree of localization is sufficient that the preservation of elastic contrast idea is not very helpful in understanding the images.

![Figure 5](image1.png)

**Figure 5.** Experimental EFTEM image and theoretical simulation (behind) for La in LaB₆ for the experimental conditions described in the text. The projected structure is indicated, and we distinguish between columns containing one (B) and two (B-B) B atoms per unit cell.

The calculations in figure 6 support the thesis. The signal detected at the exit surface (after further elastic scattering) from each atom is localized around the column in question. The signal from La is providing direct information as to the location of the La columns and is therefore chemical information and not phase contrast.

5. Quantitative HAADF or Z-contrast imaging
Atomic resolution HAADF or Z-contrast imaging in STEM is now finding application in the exploration of interfaces and defects at the atomic level. To first order, image contrast is sensitive to the atomic number, Z, of the various atomic species in the specimen. More subtly, the Debye-Waller factors of the atoms in the specimen and the detailed evolution of the elastic probe wave function also influence the HAADF images. LeBeau and Stemmer [19] made a significant advance in developing a method that allows HAADF images to be placed on an absolute scale, thus unlocking the quantitative potential of this form of imaging, especially when combined with first principles image simulations.

The method was first demonstrated on sample of SrTiO₃ [6]. Excellent agreement between experiment and calculations was obtained for a range of specimen thicknesses provided that the
simulations account for thermal diffuse scattering (TDS) to all orders i.e., all multiple thermal scattering event sequences, which the frozen phonon model effectively does.

**Figure 7.** Simulated (top half) and experimental (bottom half) PACBED pattern along [100] for a 14 nm thick region of PbWO₄.

**Figure 8.** Comparison of experimental (symbols) and simulated (line) image signals as a function of thickness. The maximum signal and minimum (“background”) signal are shown. The dashed and solid lines represent simulations without and with the effects of spatial incoherence taken into account by convolution with a 0.115 nm FWHM Gaussian.

**Figure 9.** Experimental (left panels) and simulated (right panels) images for different thicknesses (see labels). The simulated images account for finite source size (using a 0.115 nm FWHM Gaussian distribution). Note that different intensity scales are used in (a) and (b) for clarity. The uncertainties in the experimental thicknesses are ± 2-4 nm and simulated thicknesses are within ± 2 nm of the values given.
A further study was recently carried out to see if this agreement between experiment and simulation would be maintained for crystals containing heavier elements than those in SrTiO$_3$ [7]. A single crystal sample of lead tungstate (PbWO$_4$), which contains two atoms with large charge (Z = 82 for Pb, 74 for W) was used. A key step in the experiment was the accurate determination of thickness using position averaged convergent beam patterns, as illustrated in figure 7. Figure 8 shows a comparison of the experimental and simulated image signals. To model the influence of spatial incoherence, the simulated images were convolved with a Gaussian with a 0.115 nm FWHM to obtain excellent agreement between experiments and simulations. Figure 9 shows the experimental and simulated images for different thicknesses, demonstrating excellent quantitative agreement, and opening the way for quantitative Z-contrast imaging.

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