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Quantitative statistical analysis, optimization and noise reduction of atomic resolved electron energy loss spectrum images

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ABSTRACT

In this work we investigate methods of statistical processing and background fitting of atomic resolution electron energy loss spectrum image (SI) data. Application of principal component analysis to SI data has been analyzed in terms of the spectral signal-to-noise ratio (SNR) and was found to improve both the spectral SNR and its standard deviation over the SI, though only the latter was found to improve significantly and consistently across all data sets analyzed. The influence of the number of principal components used in the reconstructed data set on the SNR and resultant elemental maps has been analyzed and the experimental results are compared to theoretical calculations.

1. Introduction

Material structural and electronic properties are strongly influenced by the presence of grain boundaries, dislocations and defects. However, these types of structures provide extensive challenges for quantitative electron microscopy investigations. For example, strain and misalignments can complicate interpretation, making analysis ambiguous. Advances in microscope hardware and stability make it possible to collect electron energy loss (EEL) spectra at atomic resolution simultaneously with high angle annular dark field scanning transmission electron microscopy (HAADF STEM) images, generating what are now commonly known as STEM spectrum images (SIs). In order to prevent beam-induced damage to specimens and avoid effects of specimen drift during the long acquisition required to scan the field of interest, short dwell times are often employed. This can give rise to noisy data sets, which can further hinder interpretation.

In order to extract reliable chemical information from SI data, robust, quantitative and, ideally, automated analysis methods are required. One approach that has been proposed to remove random spectral noise is principal component analysis (PCA) (Bosman et al., 2006; Trebbia and Bonnet, 1990). PCA is a statistical technique that uses the variance of the data in different dimensions to obtain the principal components associated with the data. The data set is then reconstructed using only those principal components that provide significant information, eliminating those that represent noise. In this way, random noise in the SI can be reduced without loss of spatial or spectral resolution. PCA has been applied to atomic resolution SI data sets with considerable success (Bosman et al., 2007; Garcia-Barriocanal et al., 2010; Varela et al., 2009). Some groups have also considered removal of detector and instrumentation noise, though this is not yet routine (Thust, 2009; Riegler and Kothleitner, 2010).

While PCA has been applied in a variety of different cases and is now becoming more widely used, little is known about the statistical effects of PCA, particularly for atomic resolved images. In this work we have investigated the effects of PCA from a statistical standpoint and considered how the method affects optimal background fitting of SI data. The effect of applying PCA has been analyzed in terms of the spectral signal-to-noise ratio (SNR). In order to evaluate SIs without operator bias, automated routines for optimizing background fitting and edge integration region widths over the entire SI have been developed. The routines generate two-dimensional (2D) maps showing how the background fitting coefficients and spectral SNR vary as a function of position in the SI. As test cases, bulk ⟨1 0 0⟩ and ⟨1 1 0⟩ $SrTiO_3$ have been consid-

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ered. Our results suggest that PCA has the most significant impact on edges showing the poorest spectral SNR before PCA, such as oxygen, and that improvements in the visual quality of the atomic resolved maps are due to the reduction of spectral SNR standard deviation.

2. Methods

2.1. Theory

In order to obtain elemental maps from experimental EEL spectra, background extrapolation and edge integration are required. The basic approach for background fitting makes use of a power-law background, of the form $c(E) = AE^{-r}$ (where $c(E)$ is the recorded number of counts (background signal), E is the energy loss, and A and r are the background fit coefficients), fitted over a pre-edge energy range and then extrapolated into the edge integration range (Egerton, 1996). The extrapolated background is then subtracted from the total signal in order to obtain the characteristic edge signal. The spectral SNR is calculated from the extrapolated background and total signal in the edge integration region. Several methods for calculation of the spectral SNR have been proposed, including linear least squares (Egerton, 1982) and maximum likelihood (Unser et al., 1987) approaches. Using the linear least squares approach to calculate spectral SNR, as described by Egerton (1982), SNR is calculated as:

$$\mathrm{SNR} = \frac{I_E}{I_E + hI_B} \tag{1}$$

where I_E and I_B are the integrated edge and background signals in the edge integration region, respectively, and $h = 1 + \sigma_{I_B}/I_B$. The variance of I_B, σ_{I_B}, is calculated using the background fit coefficients and their variances, as described by Egerton (1982).

Several methods to improve the power-law background fitting and/or spectral SNR have been proposed, including using multiple pre-edge background fitting windows, 'tying' the background fitting to a region well beyond the edge energy and shifting the edge integration window to energies higher than the edge threshold (Egerton and Malac, 2002; Kothleitner and Hofer, 1998). SI data sets provide unique challenges for optimal background fitting, as the data set can consist of hundreds of individual pixel spectra. For a given edge, each pixel spectrum can have a unique background and thus optimal fitting conditions can vary from pixel to pixel. In this case, one approach is to consider all pixel spectra in the SI together in order to maximize the spectral SNR of the final elemental map, i.e., to maximize the 'global' spectral SNR. This method uses spectral SNR as an unbiased metric to determine the background and edge window widths and positions. We have developed a parallel MATLAB code that calculates the optimal background fitting and edge integration windows based on maximizing the global spectral SNR. The code calculates the spectral SNR associated with each pixel spectra for a series of edge and background window widths and edge integration window initial energies in order to find the parameters that maximize global spectral SNR. The result is that all pixel spectra have independent SNR, A and r values, fitted with background and edge windows fixed over the entire SI; finally, a mean SNR ('global SNR') and associated standard deviation can be calculated. We have implemented both the linear least squares and maximum likelihood methods for SNR calculation, however, only results using the linear least squares approach will be presented here, as this approach allows for the background to be 'tied' using a post-edge region. Details of the algorithms and implementation can be found in Appendix A. Henceforth we will use the terms SNR and spectral SNR interchangeably to refer to the spectral SNR of a single pixel spectrum, while the term global (spectral) SNR will be used to refer to the (spectral) SNR averaged over all pixel spectra in the SI. We will also refer to the standard deviation associated with the global SNR simply as SNR standard deviation.

As outlined in Section 1, PCA is a statistical technique whereby random noise can be removed by reconstructing the data using only a selected number of principal components. The details of PCA are reviewed in detail by several authors (Bonnet et al., 1999; Bosman et al., 2006; Jolliffe, 2002; Watanabe et al., 2009) and will not be covered here. When processing data with PCA, care was taken to ensure that no components containing 'significant' variation were erroneously eliminated from the reconstruction, i.e., all non-noise components were included in the reconstruction. The number of non-noise (or 'significant') components was assessed using the scree plot and score images, as described by Bosman et al. (2006). The exception to this was the cases where the data sets were processed specifically to have more or less than the 'significant' number components in order to assess the effect of the number of components on spectral SNR (Section 3.4).

2.2. Experimental

SI data was collected using an FEI Titan[3] fitted with a CESCOR probe corrector operating at 200 or 300 kV, using a dwell time of 30 ms/pixel, convergence angle of 18 mrad and collection angle of 80 mrad; drift correction was not employed during data acquisition. The 80 mrad collection angle is needed to increase the collected intensity and ensure that the full angular distribution of scattering is included so as to minimize the potential for artifacts in the interpretation of the images (Botton et al., 2010; Dwyer et al., 2008; Lazar et al., 2010). This large collection angle was achieved through a special lens series programmed in our microscope as previously discussed (Botton et al., 2010). Experimental conditions particular to the data sets analyzed are as follows: (a) bulk ⟨1 0 0⟩ $SrTiO_3$ (STO100): operating voltage of 200 kV, SI 30 pixels × 30 pixels and 0.5 eV channel width; (b) bulk ⟨1 1 0⟩ $SrTiO_3$ (STO110): operating voltage 300 kV, SI 75 pixels × 46 pixels and 1 eV channel width. Raw SI data was processed using the weighted PCA option (the default setting) of the PCA routines available as a plug-in for Digital Micrograph (Watanabe et al., 2009; HREM Research, 2011). The STO110 data was reconstructed with nine components and the STO100 data was reconstructed with five components, with the exception of the those data sets where the number of components used for the reconstruction was varied, as discussed in Section 3.4. The specimen thicknesses of both the STO100 and STO110 samples are expected to be less than 500 Å. In order to ensure appropriate interpretation of the images based on calculations, we have also done simulations at two extreme thicknesses to ensure there are no significant differences within the expected thickness range.

Making use of both the ⟨1 0 0⟩ and ⟨1 1 0⟩ orientations of $SrTiO_3$ provides us with the opportunity to investigate the effect of stoichiometry on elemental mapping and background fitting, as the ⟨1 0 0⟩ unit cell contains Sr, Ti–O and O columns, while the ⟨1 1 0⟩ unit cell contains Sr–O, Ti and O–O columns (where the notation O–O is used to indicate the presence of two O atoms per unit cell, while Sr–O, Ti–O and O are used to indicate the presence of one O atom per unit cell).

2.3. Simulations

Simulations of HAADF STEM images were conducted using a frozen phonon multislice approach (Kirkland, 2010), adapted for speed to run on the multi-threaded architecture of the graphics processing unit (GPU) (Dwyer, 2010). The calculations used supercells of size approximately 30 Å × 30 Å sampled by 512 pixels × 512 pixels, and incorporate the qualitative effects of source size by convolution with a Gaussian of 1 Å