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Analysis and Artifacts in EELS Spectrum Imaging

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Aberration-corrected electron microscopes now make it practical to record two-dimensional maps of composition and bonding at atomic resolution [1]. With earlier instruments, where only a handful of spectra could be recorded, each spectrum could be inspected individually, leading to a direct and simple analysis of trends in bonding and composition. The large data sets that result from EELS-SI at atomic resolution present new opportunities and challenges. More data from similar regions means better estimates of confidence levels. EELS spectra recorded less than a nm from an interface can show new and non-bulk fine structure features that were not detectable with larger probe sizes and cannot be easily fingerprinted. However, many of the unbiased multivariate data analysis methods such as the popular principle component analysis (PCA)[2,3] can fail to detect such changes under typical conditions, although they do lead to dramatic reductions in the apparent noise.

Our goal here is to identify and, if possible, correct the conditions under which PCA and similar methods can fail. PCA is an optimal algorithm in the sense that it provides the least number of orthogonal vectors that capture a given percentage of the image variance. Unfortunately, the poor peak-to-background ratio in EELS means that much of that variance arises from changes in slope and shape of the background, rather than the edge of interest. The result is that the usual approach of using a scree plot to determine the number of significant components can grossly underestimate the number of significant components needed to describe the data. Fig 1 shows the consequences of PCA filtering raw data to remove noise – here retaining 10 components, 7 more than indicated by the scree plot. The true structure of the Al-K edge is lost and replaced by an artifact that tracks the tails of the preceding La-M edge instead (Fig 1b). For EDS and SIMS where backgrounds are very low compared to the signal, weighting the data by two-way scaling can improve the situation [4,5]. Unfortunately for EELS, weighting fails where most needed: in the limit of a vanishingly small signal on a large background, the scaling asymptotes back to the unweighted approximation. This effect is particularly pronounced when examining PCA filtered EELS fine structure (Fig 2), which is often systematically distorted, with peaks shifting as much an electron volt. We have also found cases where the interface states themselves have been filtered away completely (Fig 3).

The failure is not PCA itself, but rather the global metric of total image variance. For instance, in an *NxN* pixel image, a line of interface states only accounts for 1/N of the total image pixels. As $N \rightarrow \infty$, the fraction of image variance contained in the interface states tends to 0, and its PCA rank will drop below that of bulk noise components. Employing *a-priori* knowledge of model-based approaches [6], or local metrics such as spatially resolved residuals often overcome these problems. Local minimizations, such as Multivariate Curve Resolution [5] can also be effective. [7]

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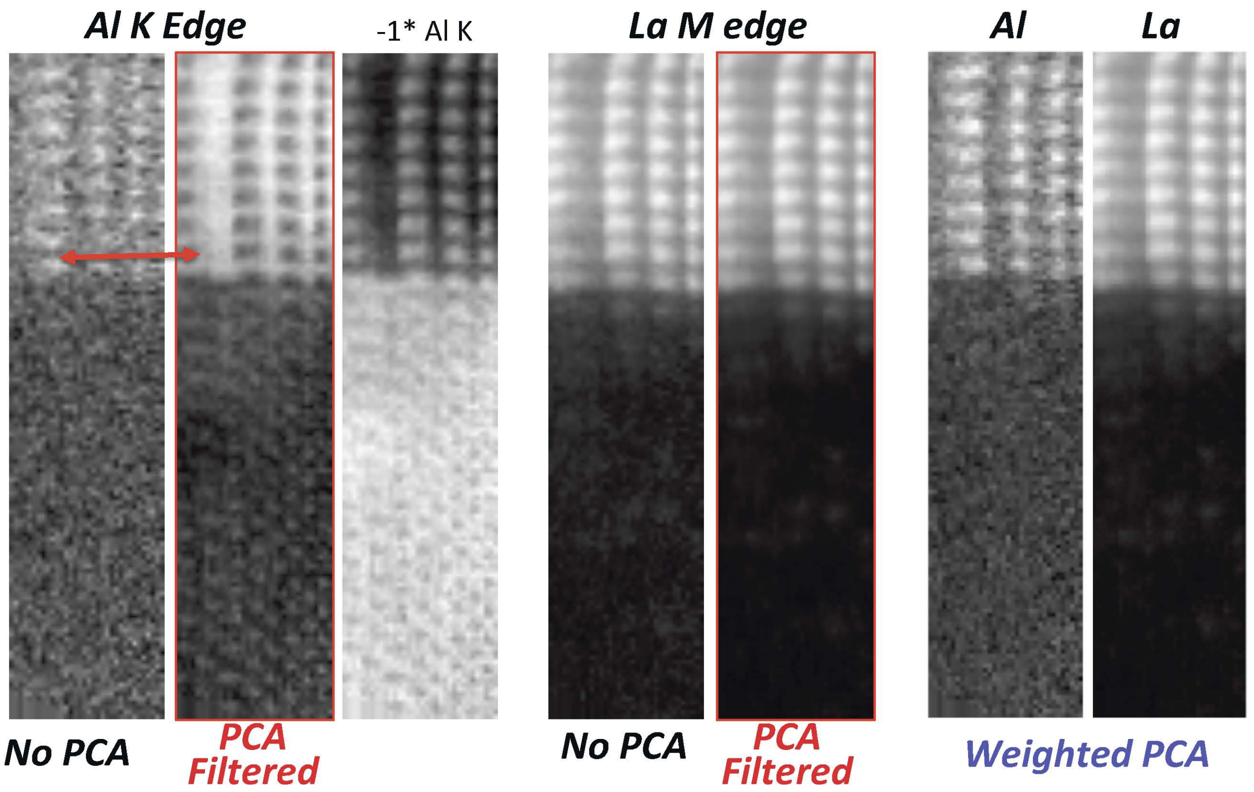
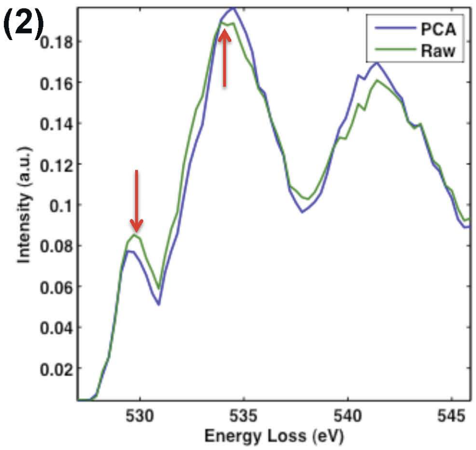


Figure 1. The Al-K and La-M Edges recorded across a $SrTiO_3/LaAlO_3$ interface. The power-law subtracted and edge integration is applied or raw data (no PCA) and PCA-filtered (1^{st} ten components) data sets. While the unfiltered Al-K edge shows the Al lattice correctly, the PCA-filtered data shows a contrast pattern that tracks the La-M edge contrast reversed, along with a false periodicity in the $SrTiO_3$ substrate. A weighted PCA (again 10 components) is able to restore a more plausible Al-K map. Here again the scree plot failed to provide a reliable cutoff (it would predict 3). With a slightly noisier image, the weighted PCA would have failed as well, producing similar artifacts to unweighted PCA.



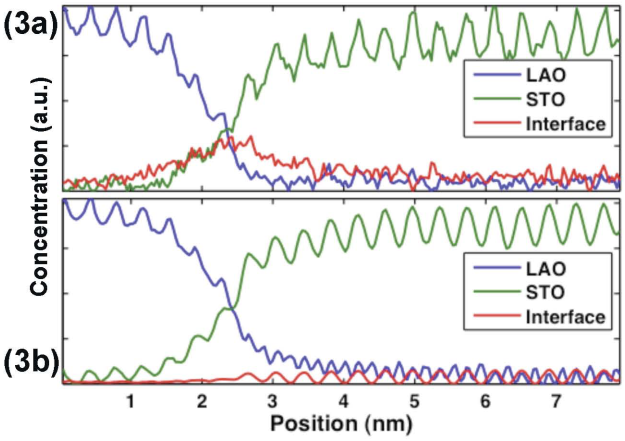


Figure 2. The O-K edge summed over 20 spectra recorded at a $SrTiO_3/LaAlO_3$ interface. If the raw data is PCA filtered prior to background subtraction, the shape of fine structure is altered, with the first and second peaks shifting strongly in opposite directions by -0.4 eV, +0.4 eV respectively.

Figure 3. Three-component multivariate curve resolution (MCR) of the O-K edge across a $SrTiO_3/LaAlO_3$ interface. The MCR fit to the raw data (a) shows a clear interfacial component that is also apparent in the raw spectra, but is lost by weighted PCA filtering (b) the raw data prior to background subtraction. The weighted data (b) also displays unphysical intensity oscillations in the LAO and “interface” components.