Removing the effects of elastic and thermal scattering from spectrum images

NR Lugg[1,2], MJ Neish[1], M Haruta[3], SD Findlay[4], K Kimoto[3], T Mizoguchi[5], G Kothleitner[6], W Grogger[6], F Hofer[6], LJ Allen[1]

[1]School of Physics, The University of Melbourne, Parkville, Victoria 3010, Australia
[2]Institute of Engineering Innovation, The University of Tokyo, Tokyo 116-0013, Japan
[3]National Institute for Materials Science, 1-1 Namiki, Tsukuba, Ibaraki 305-0044, Japan
[4]School of Physics, Monash University, Clayton, Victoria 3800, Australia
[5]Institute of Industrial Science, University of Tokyo, Tokyo 153-8505, Japan
[6]FELMI, Graz University of Technology, Steyrergasse 17, 8010 Graz, Austria

Scanning transmission electron microscopy (STEM) has shown great promise in mapping the location and species of atoms in technologically interesting materials using electron enegy-loss spectroscopy (EELS) [1-3] and, more recently, energy-dispersive x-ray (EDX) spectroscopy [4]. Both techniques however allow for more powerful analyses than qualitative elemental mapping.

In EELS, by studying the electron energy-loss near-edge structure (ELNES), one is not only able to map the location and species of elements, but also their bonding states [5,6]. Specifically, there has been much interest in mapping changes in the bonding states of oxygen in transition metal oxides – at atomic-resolution – by studying the ELNES, since the spectra of inequivalently bonded oxygen also atoms contain information on the bonding states of the transition metals. However, due to the strong elastic and thermal scattering of the electron probe, spectra from inequivalently bonded oxygen atoms become mixed for any probe position and therefore any direct relation between recorded spectra and actual inequivalent spectra becomes difficult to obtain.

Atomic resolution EDX is a promising technique in quantitatively mapping the concentration of elements in a material due to the localized nature of the scattering potential. But even so, the elastic and thermal scattering of the probe still cause a highly nonlinear relation between x-ray counts and elemental concentrations [7], seemingly reducing the usefulness of EDX in such quantitative analyses.

Recently however, a technique has been developed whereby one is able to deconvolve the elastic and thermal scattering of the electron probe from experimental data [8], making ELNES spectra directly interpretable and putting EDX data on a quantitative scale. Here we present the theory behind this technique and a step-by-step method of how to implement it using the quantum excitation of phonons model [9] to model the elastic and thermal scattering of the probe and the conjugate gradient least squares (CGLS) algorithm to solve the deconvolution problem. Furthermore, we present results having applied this method to both experimental ELNES [10] and EDX [11] data for $SrTiO_3$.

[1] K Kimoto et al, Nature 450 (2007) 702
[2] M Bosman et al, Phys. Rev. Lett. 99 (2007) 086102
[3] DA Muller et al, Science 319 (2008) 1073
[4] AJ D'Alfonso et al, Phys. Rev. B 81 (2010) 100101

[5] H Tan et al, Phys. Rev. Lett. 107 (2011) 107602
[6] M Haruta et al, Appl. Phys. Lett. 100 (2012) 163107
[7] BD Forbes et al, Phys. Rev. B 86 (2012) 024108
[8] NR Lugg et al, Appl. Phys. Lett. 101 (2012) 183112
[9] BD Forbes et al, Phys. Rev. B 82 (2010) 104103
[10] MJ Neish et al, Phys. Rev. B 88 (2013) 115120
[11] G Kothleitner et al, Phys. Rev. Lett. (2014) accepted

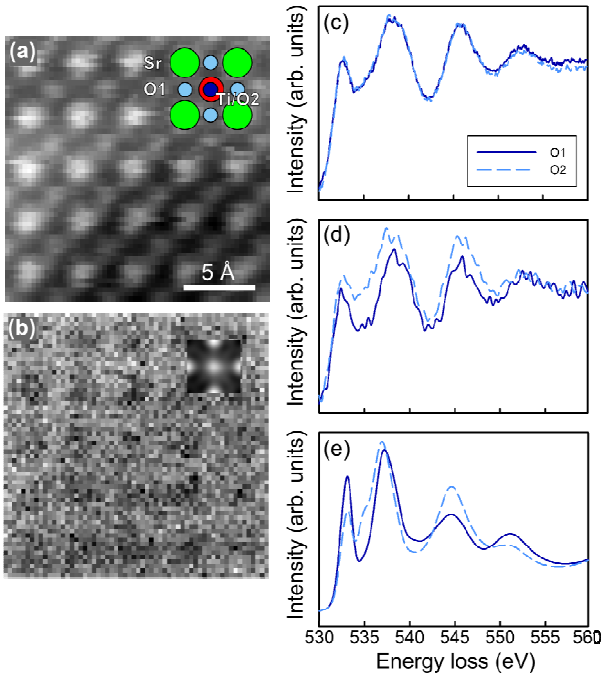

Figure 1 (a) HAADF image with the projected structure of $SrTiO_3$ in the [001] orientation. In projection, the oxygen atoms labelled O1 and O2 are inequivalently bonded to the surrounding atoms. (b) Background-subtracted EELS map integrated over 535 to 560 eV, with the inelastic scattering potential obtained after inversion overlaid. (c) EELS spectra obtained from the background-subtracted data. (d) EELS spectra obtained after inversion. (f) EELS spectra calculated using WIEN2k. Shifts in peak positions for the two O columns are observed only after removing the effects of the scattering of the incident probe, which agrees with the first-principles WIEN2k calculation.

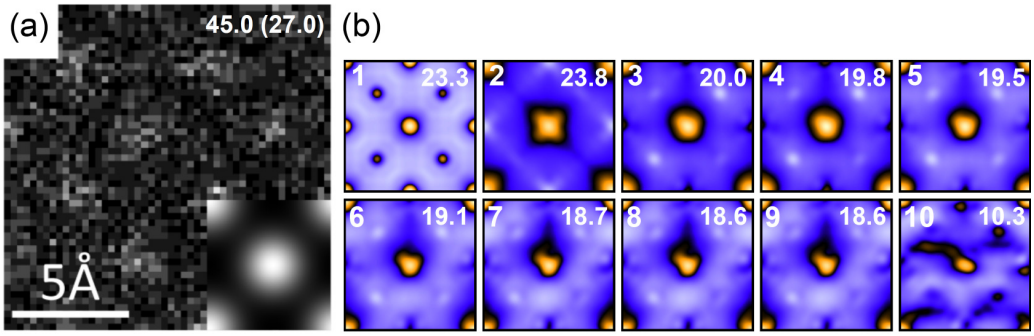

Figure 2 (a) Experimental atomic resolution EDX elemental map for $SrTiO_3$ for the Sr K shell, calibrated with data taken under non-chanelling conditions. Numbers correspond to the density of Sr in $SrTiO_3$ (in atoms/nm^3) after averaging the entire map (averaging only around Sr columns). Simulation inset. (b) EDX scattering potential of the Sr K shell as a function of CGLS iteration number (1–10). Integrating the potenial and multiplying the thickness yields a density (indicated on each subfigure). Convergence is achieved in the region of 7–9 iterations and deteriorates due to noise thereafter. The nominal density is 16.8 atoms/nm^3.