

## The quest for quantitative analytical microscopy at atomic resolution

L.J. Allen<sup>1</sup>, A.J. D'Alfonso<sup>1</sup>, S.D. Findlay<sup>2</sup>, W. Grogger<sup>3</sup>, M. Haruta<sup>4</sup>, F. Hofer<sup>3</sup>, J. Hwang<sup>5</sup>, K. Kimoto<sup>4</sup>, G. Kothleitner<sup>3</sup>, N.R. Lugg<sup>1</sup>, T. Mizoguchi<sup>6</sup>, M.J. Neish<sup>1</sup>, J.Y. Zhang<sup>5</sup>, S. Stemmer<sup>5</sup>

<sup>1</sup>School of Physics, University of Melbourne, Parkville, Victoria 3010, Australia

<sup>2</sup>School of Physics, Monash University, Clayton, Victoria 3800, Australia

<sup>3</sup>FELMI, Graz University of Technology, Steyrergasse 17, 8010 Graz, Austria

<sup>4</sup>National Institute for Materials Science, 1-1 Namiki, Tsukuba, Ibaraki 305-0044, Japan

<sup>5</sup>Materials Department, University of California, Santa Barbara, California 93106-5050, USA

<sup>6</sup>Institute of Industrial Science, University of Tokyo, Tokyo 153-8505, Japan

Modern aberration-corrected electron microscopes are capable of a range of analytical techniques for atomic resolution materials analysis. In scanning transmission electron microscopy (STEM) mode, Z-contrast imaging is routinely used and in recent years has become a quantitative technique. New detectors optimized for rapid x-ray collection in STEM enable energy dispersive x-ray (EDX) spectral mapping at the atomic scale. Electron energy loss spectroscopy (EELS) permits the user to collect low-loss and core-loss spectrum images as a function of probe position, providing complementary analytical information to EDX mapping. These techniques are made more powerful when coupled to an understanding of the elastic and inelastic scattering processes underlying the measured signals.

The advent of quantitative Z-contrast imaging [1] led to the counting of atoms in a gold foil [2] and, more recently, has culminated in the three-dimensional imaging of individual dopant atoms within small clusters, containing 4–5 Gd atoms, in SrTiO<sub>3</sub> [3]. In that work, uncertainties in the depth locations of individual dopants were less than 1 unit cell. Some of these results are shown in Fig. 1. The complete 3D configuration of dopant atoms can be determined from single quantitative STEM images, along with information on expectation values and dopant visibility. Sufficiently thin TEM foils are key for an unambiguous interpretation of data.

Elemental mapping using energy-dispersive x-ray spectroscopy in scanning transmission electron microscopy, a well-established technique for precision elemental concentration analysis at submicron resolution, was first demonstrated at atomic resolution in 2010 [4] and this has progressed rapidly [5]. However, to date atomic resolution elemental maps have only been interpreted qualitatively because the elastic and thermal scattering of the electron probe confounds quantitative analysis. Accounting for this scattering, absolute scale quantitative comparisons between experiment and quantum mechanical calculations for EDX elemental maps have been made [6]. The only consideration to date of quantitative STEM EELS elemental mapping is the work in Ref. [7]. In this work [6], EELS maps were acquired simultaneously, facilitating a direct comparison between the two modes of imaging.

In STEM EELS fine structure experiments on crystalline specimens, information concerning atoms of the same species that are not equivalently bonded is often mixed together by the effects of elastic and thermal scattering of the probe. A method has recently been developed to effectively deconvolve the incident probe from the experimental signal [8]. This allows one to unmix the spectra from different atom types and to make valid comparisons with fine structure calculations using standard packages, which usually do not contain these effects [8-10].

## References

- [1] J.M. LeBeau et al., Phys. Rev. Lett. 100 (2008) 206101.
- [2] J.M. LeBeau et al., Nano Lett. 10 (2010) 4405.
- [3] J. Hwang et al., Phys. Rev. Lett. 111 (2013) 266101.
- [4] A.J. D'Alfonso et al., Phys. Rev. B 81 (2010) 100101(R).
- [5] L.J. Allen et al., MRS Bulletin 37 (2012) 47.
- [6] G. Kothleitner et al., submitted for publication.
- [7] Xin, H.L. et al., arXiv:1110.5018.
- [8] N.R. Lugg et al., Appl. Phys. Lett., 101 (2012) 183112.
- [9] M. Haruta et al., J. Appl. Phys., 114 (2013) 083712.
- [10] M.J. Neish et al., Phys. Rev. B 88 (2013) 115120

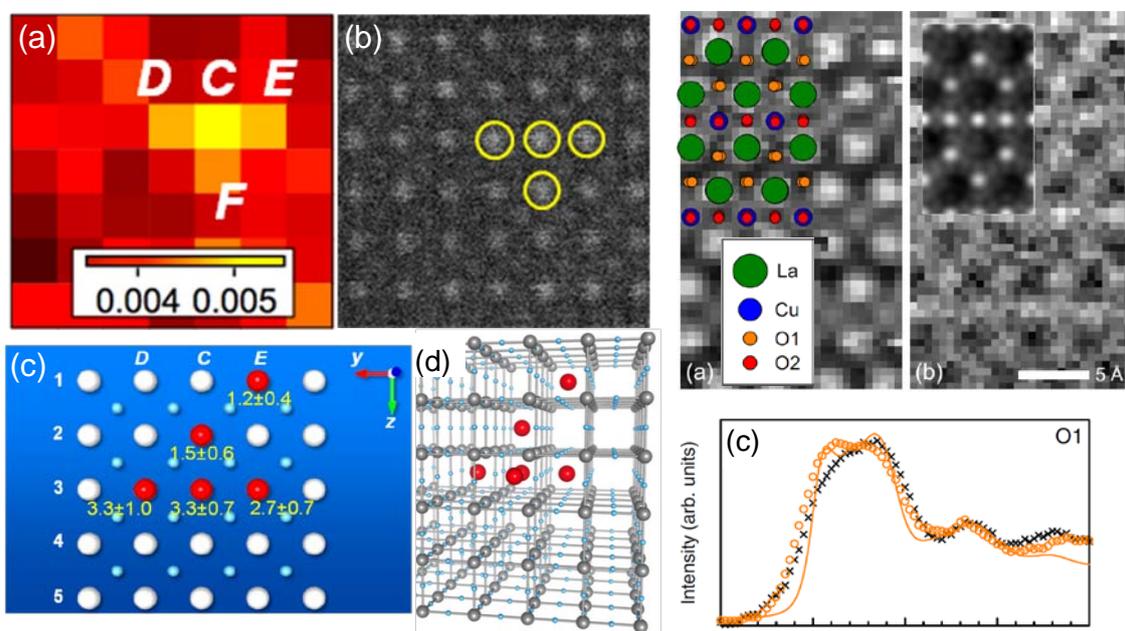


FIG. 1. (a) Derived intensity maps on the nominal Sr columns in  $\text{SrTiO}_3$  from the Z-contrast image in (b). (c) Schematic of the number and positions, of Gd impurity atoms in the columns labeled D C and E in (a), obtained using simulations in tandem with a careful analysis of the data. (d) 3D illustration of the area in (a) with the most probable Gd dopant configuration in columns C–F. For clarity, Sr atoms are not shown and some Ti and O atoms were also removed.

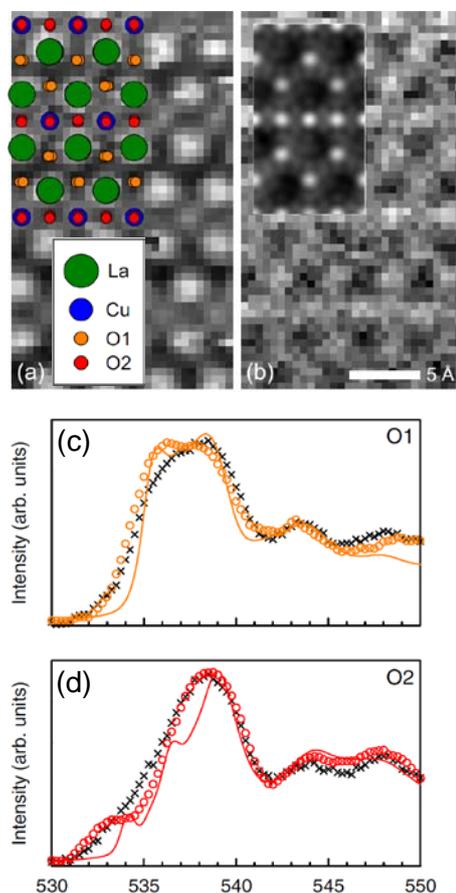


FIG. 2. (a) HAADF image with projected structure of  $\text{La}_2\text{CuO}_4$  overlaid, taken concurrently with the EELS signal. (b) Background-subtracted EELS map integrated over 536–586 eV, with potential obtained by inversion overlaid. Spectra obtained from the (c) O1 and (d) O2 columns from the background-subtracted experimental data cube (crosses) and the data cube obtained by inversion (circles). Spectra calculated using WIEN2K are also shown (solid lines).