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# Simulation in elemental mapping using aberration-corrected electron microscopy

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## ABSTRACT

Elemental mapping at the atomic scale in aberration-corrected electron microscopes is becoming increasingly widely used. In this paper we describe the essential role of simulation in understanding the underlying physics and thus in correctly interpreting these maps, both qualitatively and quantitatively.

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## 1. Introduction

The use of electron energy-loss spectroscopy (EELS) to determine the valence of an atom occupying a particular crystal lattice site was demonstrated by Taftø and Krivanek in the early 1980s [1]. Pioneering developments in instrumentation for EELS and energy-loss imaging and the design and implementation of a post-column imaging filter are described in papers by Ondrej Krivanek and co-workers in the early 1990s [2,3], with the stated aim of fast imaging and elemental mapping in scanning transmission electron microscopy (STEM) mode. This led to a number of milestones and ideas relating to EELS and elemental mapping in which Ondrej Krivanek played a pivotal role. These include an exploration of spatial resolution in energy-filtered transmission electron microscopy (EFTEM) elemental maps [4]; the spectroscopic imaging of a single atom within a bulk solid using STEM [5]; an exploration of annular dark-field (ADF) imaging and EELS at low primary energies [6]; and atom-by-atom structural and chemical (elemental) analysis using ADF imaging [7].

This pioneering work, together with the development of aberration-corrected electron microscopy, another area to which Ondrej Krivanek has made major contributions, has led to elemental mapping at the atomic scale becoming a widely used technique. Elemental mapping in two dimensions at atomic resolution in STEM, using EELS based on inner-shell ionization, was first demonstrated in 2007 [8,9] and rapidly evolved as a useful tool –

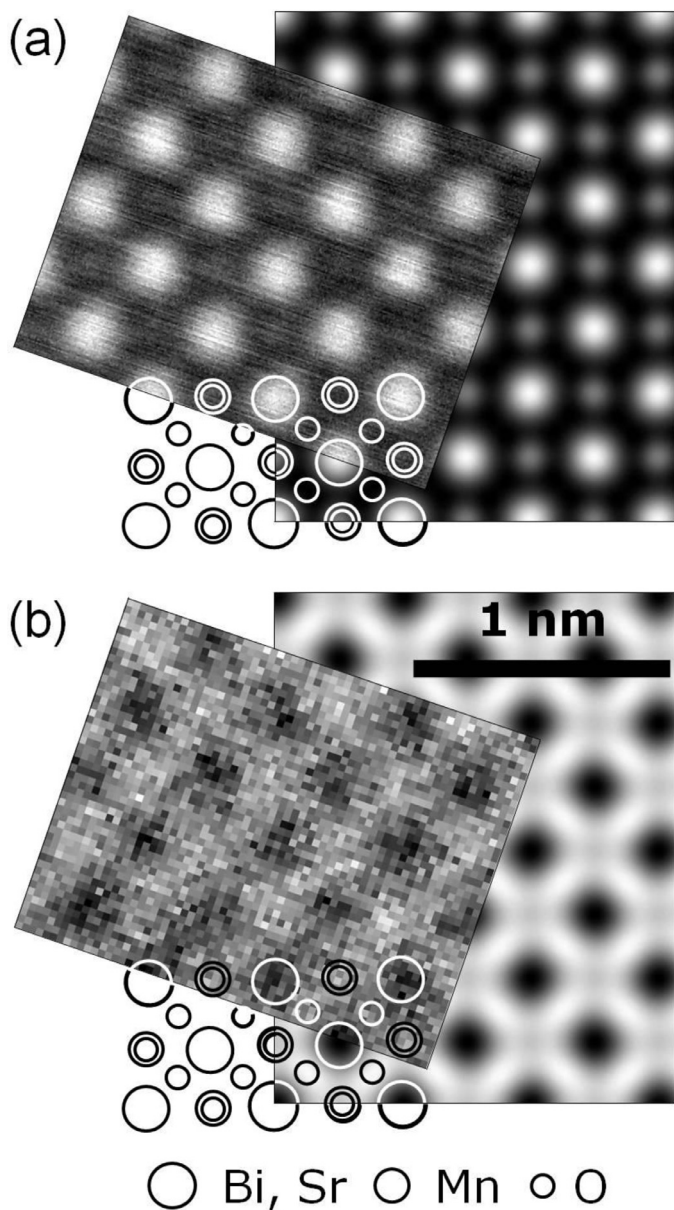
see for example [10–14] where, in particular, Ref. [13] is a comprehensive review of atomic-resolution core-level spectroscopy in STEM. The rest of this review will focus on elemental mapping in two dimensions and, in particular on understanding the physics behind such maps via simulation. For more general discussion of STEM EELS the reader is referred to Refs. [15,16].

Unless the detector collection angle is very large, EELS is a partially-coherent imaging mode – by which we mean that it depends not only on the probe intensity distribution but also on its phase – and this may hinder a simple direct interpretation of the elemental maps. In STEM EELS we integrate up over a suitable energy-loss window to form an elemental map. In Fig. 1(a) we show a Z-contrast image of  $\text{Bi}_{0.5}\text{Sr}_{0.5}\text{MnO}_3$  oriented along the  $\langle 001 \rangle$  direction, extracted from one of the seminal STEM EELS papers [8]. Columns containing Bi and Sr atoms are clearly evident, as are columns containing both Mn and O atoms. Since the Z-contrast signal scales roughly as  $Z^2$ , the pure O columns are not evident in the image. However, the O columns can be seen by integrating the signal obtained for the O K-edge in an EELS spectrometer over an energy window of 30 eV above the ionization threshold, as can be seen in Fig. 1(b), also extracted from Ref. [8]. The data in Fig. 1 were acquired using the VG HB501 scanning transmission electron microscope at the SuperSTEM facility in the UK, a system fitted with a Nion spherical aberration corrector.

As an alternative to STEM EELS one can use energy-dispersive X-ray (EDX) analysis, detecting the X-rays which are emitted subsequent to ionization as the STEM probe is scanned across the specimen. Since EDX elemental mapping is an incoherent mode

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**Fig. 1.** Comparison between experiments (the tilted images) and simulations of  $\text{Bi}_{0.5}\text{Sr}_{0.5}\text{MnO}_3$  oriented along the [001] zone axis. (a) Z-contrast, (b) the O K-edge EELS elemental map. The atomic structure is indicated. The EELS elemental map was generated by integrating the EELS spectra over a 30 eV window above the ionization threshold. The simulations assume a 330 Å thick sample. Experimental details are given in Ref. [8].

of imaging, image interpretation may be expected to be simpler than for EELS. In STEM EDX we are detecting X-rays generated when holes are filled post ionization and all possible kinematics associated with ionization are sampled, since there is no detector aperture as in EELS to exclude electrons inelastically scattered to larger angles. Therefore, the cross section for EDX is proportional to that for an EELS detector spanning the whole solid angle and integrated up over all possible energy losses. Furthermore, the larger effective energy window in EDX, relative to the smaller window usual in EELS, leads to an increased localization of the signal in an EDX elemental map. Thus EDX imaging is more reminiscent of the widely used technique of ADF or Z-contrast imaging, but with the advantage that elemental information is directly available for a range of different elements and X-ray peaks. A further advantage of EDX mapping relative to EELS is the accessibility of higher

energy-loss peaks and their associated increased localization. The first two-dimensional atomic resolution elemental maps based on EDX were published as recently as 2010 [17,18] and considerable improvements in the quality of such data followed rapidly [19], although signal-to-noise ratios are generally lower than for EELS. Quantification in STEM EDX has recently been addressed [20–23].

Elemental maps displaying features at atomic scale can also be obtained in conventional transmission electron microscopy (CTEM) in EFTEM mode, see for example Ref. [24], and in later work the advent of chromatic aberration correction facilitates this greatly [25,26]. However, quantum mechanical calculations from first principles need to be done in tandem with the experiments to understand the physical information encoded in the images; in particular this need is due to the preservation of elastic contrast. Ways of ameliorating the preservation of elastic contrast have recently been proposed [27].

Understanding the effects of the channelling and thermal diffuse scattering of the probing electrons on elemental maps is key to their correct interpretation, particularly for crystalline specimens. For example, it may be tempting to assume that a STEM probe, when positioned above a particular column of atoms in a specimen, interacts only with that column and, furthermore, in a uniform way with all atoms in the column. This is only reasonable in the limit of a thin specimen, with the probe focused on or near the entrance surface. It is not generally appreciated that, for elemental maps based on less tightly bound atomic orbitals, the ionization interaction can be quite delocalized and that ionization may occur even when the probe intensity on a particular atom is small [28,29]. In loose terms, the atom reaches out to the probe. Furthermore, thermal diffuse scattering can lead the unwary to interpret an elemental map as either suggesting too few [8] or too many [30] atoms of a particular species in an atomic column. Atomic scale elemental maps are not necessarily atomic resolution maps in the sense that they directly and quantitatively map where the atoms are and what they are. Therefore, simulations are an essential part of confidently making correct interpretations of elemental maps. In the next section we will discuss the theoretical framework for such simulations.

## 2. Inner-shell ionization in the quantum excitation of phonons model

A general scheme to calculate elemental maps is provided by working within the context of the quantum excitation of phonons (QEP) model [31,32]. An important feature of the QEP model is that signals based on ionization arising from both elastically and thermally scattered electrons can be calculated separately and this can yield important physical insights.

The fraction of the incident electrons that are involved in ionization events associated with a particular edge may be expressed in the form [31,33]:

$$F(\mathbf{P}) = \frac{2\pi}{\hbar v} \sum_{j,i} \iint \psi_{0,j}^*(\mathbf{P}, \mathbf{r}, z_i) W_j(\mathbf{r}, \mathbf{r}', z_i) \psi_{0,j}(\mathbf{P}, \mathbf{r}', z_i) d\mathbf{r} d\mathbf{r}'. \quad (1)$$

The functional dependence denoted by  $\mathbf{P}$  in Eq. (1) represents the probe position  $\mathbf{R}$  on the surface of the specimen in STEM and in CTEM it could represent the tilt of the incident beam specified by the tangential component of the wave vector of the incident electrons  $\mathbf{k}_{0t}$ . The speed  $v = \hbar k_0/m$ , with  $k_0$  the wave number of the incoming electron and  $m$  its mass. The summation over  $i$  is over slices in the specimen and that over  $j$  refers to different possible atomic configurations “seen” by the incident electron in the QEP model. The “auxiliary functions”  $\psi_{0,j}(\mathbf{P}, \mathbf{r}, z_i)$  associated with the probing electron, and where the co-ordinate  $\mathbf{r}$  refers to a plane perpendicular to the optical axis, are calculated for the particular atomic configuration labelled by  $j$ . The nonlocal potentials in

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