doi:10.1017/S1431927613011550
Microsc. Microanal. 19 (Suppl 2), 2013

Quantification of Cation Ordering in $La_{2-2x}Sr_{1+2x}Mn_2O_7$ by STEM EELS

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The properties of $La_{2-2x}Sr_{1+2x}Mn_2O_7$ (LSMO) vary not only by the composition, defined by x, but also the local ordering of La and Sr. Using scanning transmission electron microscopy (STEM) combined with electron energy loss spectroscopy (EELS) we will examine the ordering of three different samples with x = 0.36, 0.50 and 0.56. Using a Nion UltraSTEM, equipped with a 5th order aberration corrector and operating at 200kv, STEM EELS images of individual atomic columns are easily resolved. While it is possible to gain a qualitative picture of the degree of La/Sr ordering from such images, detailed quantification is complicated by the delocalized nature of the EELS scattering potential and beam spreading as the probe propagates through the specimen. We will present quantitative methods for determining the degree of disorder in these specimens using corrections for these effects based on the simulation of STEM EELS images [1, 2].

To describe La/Sr ordering within LSMO we define planes A and B as shown in the projected structure in Fig. 1. We then use the parameter a to quantify the order by expressing the structure as in terms of these planes as $La^{A}_{(1-a)}La^{B}_{2(0.5-x+0.5a)}Sr^{A}_{a}Sr^{B}_{2(0.5+x-0.5a)}Mn_2O_7$. For example, for x = 0.5 we may write $La^{A}_{(1-a)}La^{B}_{a}Sr^{A}_{a}Sr^{B}_{2(1-0.5a)}Mn_2O_7$. For a = 0, all La resides on the A planes and all Sr on the B planes, while a value of a = 2/3 corresponds to a random distribution of La and Sr.

As a first step in the quantification process we use the procedure shown schematically using simulated EELS images based La M_{45} and Sr L_{23} EELS signals, in Fig. 1 for the case of x = 0.5 and a= 0. Each image is first divided by its mean in order normalize for ionization differing cross sections. These images are then summed using the nominal composition, in this case La + 2Sr to form a "total" image. We then determine fractional images by dividing each normalized image by the total image. A first attempt at quantification, without theoretical corrections, can be obtained by averaging along the planes. The La (green) and Sr (red) averaged signals are shown in the plot in Fig. 1. A first guess of the ordering might naively be obtained by comparing the peak heights above each plane. For example in this case, it is seen that ~20% of the signal on the A plane comes from the Sr L shell, despite the fact that no Sr is present in this plane. It is this discrepancy that which we aim to correct.

While it would be possible to tabulate corrections to experimental measurements using this technique, the extraction of the signal summed along the planes is time consuming, especially if the scan directions are not aligned with the unit cell, or there is significant drift during the image acquisition. The accuracy of such a measurement is also limited by experimental noise, requiring averaging over a significant field of view.

In order to simplify the quantification process make use of the fact that the contrast of the fractional images is reduced as disorder is increased. This is shown using simulations in Fig.2. In addition we

choose a simple measure of contrast, the standard deviation divided by the mean. This "normalized" standard deviation can be quickly determined with little user input and is easily automated. In addition it is insensitive to scan alignment and moderate drift. As seen in Fig. 2, the variation of this quantity is almost linear in a. While we have determined that this measure is insensitive to source size corrections, it can be seen in Fig. 2 that the specimen thickness still needs to be determined independently. The accuracy of the thickness determination provides a limit on the accuracy of the disorder determination.

While the use of the reduction in contrast provides an empirical solution applicable to this system and similar planar samples, these sorts of corrections can also be applied in a more general, if more time consuming manner for samples with other geometries. Automated methods of locating intensity peaks and measuring peak heights offer the possibility of extending the use of theoretical quantification corrections to many diverse specimens.

References:

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[3] This work was supported in part by DOE Grant No. DE-FG02-09R46554 (M.P.O.), by the DOE Office of Basic Energy Sciences, Materials Sciences and Engineering Division (S.J.P.,M.V.) and by the European Research Council Starting Investigator Award (MR).

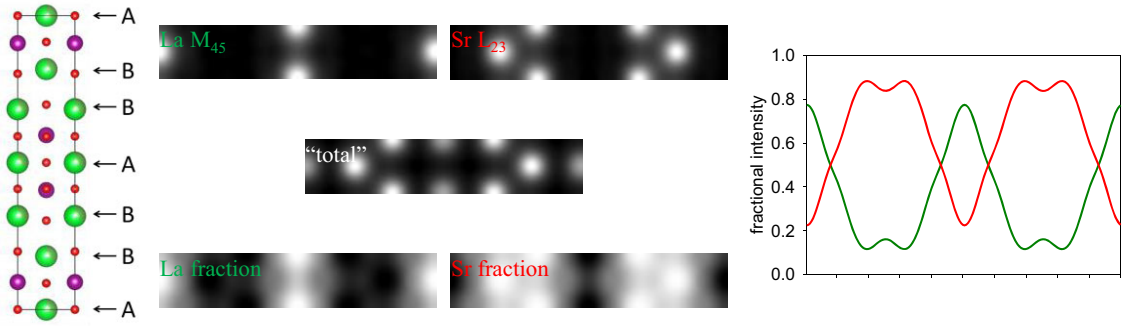

Figure 1. Projected structure of LSMO and simulated images for x = 0.5, a = 0. Fractional images are formed as described in the text and averaged vertically.

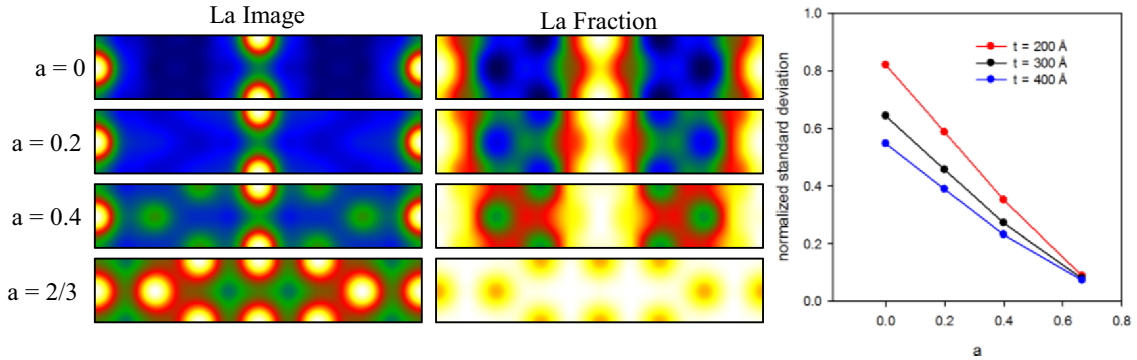

Figure 2. Variation of the La M-shell EELS image and fractional image for x = 0.5 for varying a. The normalized standard deviation is plotted as a function of a for three different thicknesses.

https://doi.org/10.1017/S1431927613011550 Published online by Cambridge University Press