Tan *et al.* Reply: The authors of [1] comment on our Letter [2] based on calculated electron energy-loss spectroscopy (EELS) spectra using density functional theory (DFT). They argue that the tetrahedral symmetry at the Mn^{2+} site in Mn_3O_4 differs significantly from the octahedral symmetry in our MnO reference sample which causes us to wrongly interpret the energy-loss near-edge structure (ELNES) changes as intermixing, while they are really caused by a symmetry change. We will explain why we think this explanation is unjustified.

The authors simulated the Mn^{2+} L_3 ELNES in tetrahedral (Mn_3O_4) and octahedral (MnO) coordination and found that the upper shoulder (peak *c* in Fig. 1 of the Comment [1]) in the tetrahedral coordination is slightly more pronounced than in the octahedral coordination. To estimate the influence of the coordination on the ELNES signature in the case of Mn^{2+}, we acquired an EELS spectrum for T_d Mn^{2+} in MnV_2O_4 (Fig. 1). Even though shoulder *c* is more pronounced in the case of tetrahedral coordination as compared to octahedral coordination (MnO), it is clear that coordination alone cannot account for the discrepancy between the measured signal at the Mn^{2+} site in Mn_3O_4 and the Mn^{2+} references. This trend was also observed experimentally [3]. Slight geometrical differences between various Mn^{2+} compounds are known to result in subtle differences in the ELNES signature [4]. Indeed, the authors calculate a 20% increase in intensity under peak *c* due to geometrical effects in the case of tetrahedral Mn^{2+} in Mn_3O_4. However, even a 20% increase of peak *c* cannot explain the larger discrepancy between the signal measured at the Mn^{2+} site and the references for
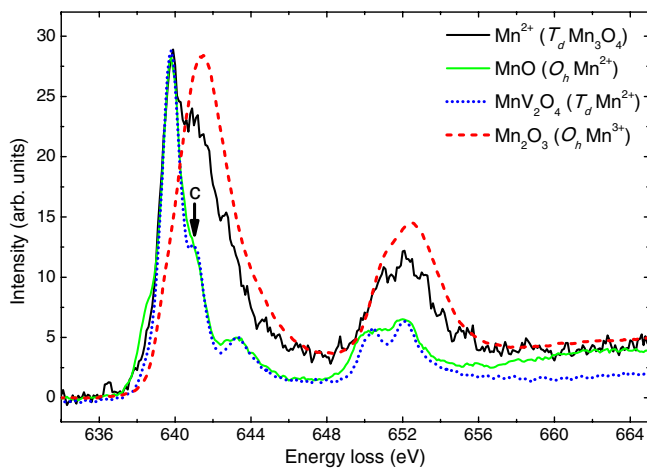
Mn^{2+} in our work. In summary, we experimentally show that Mn L_3 ELNES differences due to symmetry or geometry are only secondary effects, and that intermixing of the signal from neighboring columns is dominant.

Signal intermixing has been shown to be due to a combination of inelastic delocalization, elastic scattering, and source size broadening [5,6]. All of these effects were included in our simulations, and a remarkable agreement was obtained with the experiment [2]. The authors quote a simple model of delocalization $d_E = 0.5\lambda/\theta_E^{3/4}$, providing a value of 1.4 Å at our experimental conditions [7,8] and leading to the conclusion that intermixing should be negligible here as this value lies below the smallest interatomic distance between two Mn columns. This simple model, however, neglects the crucial elastic propagation of the electrons through the finite thickness of the sample [2,9]. On top of this, source size broadening further mixes the signals from neighboring columns and must also be taken into account [10]. Other authors have shown similar phenomena: Botton *et al.* compared simulated and experimental Ba $M_{4,5}$ signal maps at a $BaTiO_3$-$SrTiO_3$ interface [11] and showed that the Ba signal is still 30% at a distance of 3 Å away from the interface in both experiment and simulation. These considerations show the dominant role of intermixing in atomic resolution EELS experiments.

In summary, we agree that symmetry or geometry effects have an impact on the shape of the Mn ELNES, but we have demonstrated that the role of this effect is secondary as compared to signal intermixing between two sites with different formal valence in our experiments.

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FIG. 1 (color online). ELNES signature from the Mn^{2+} site in Mn_3O_4 in comparison to signatures for Mn in different oxidation states and coordinations. Note the subtle effect of coordination on the ELNES of MnO and MnV_2O_4 and the large discrepancy between the Mn^{2+} site signal and the Mn^{2+} references. The coordination effect is too small to explain the spectrum observed at the Mn^{2+} site in Mn_3O_4. Signal intermixing between the Mn^{2+} and Mn^{3+} sites seems a more plausible explanation.

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