

## Comment on “2D Atomic Mapping of Oxidation States in Transition Metal Oxides by Scanning Transmission Electron Microscopy and Electron Energy-Loss Spectroscopy”

2 Tan *et al.* [1] communicated experimental evidence for local differences of the electronic structure near crystallographically distinct transition metal sites in  $\text{Mn}_3\text{O}_4$  using spatially resolved electron energy-loss spectroscopy (EELS). They interpreted the EEL spectra of  $\text{Mn}^{2+}$  and  $\text{Mn}^{3+}$  sites in terms of the Mn  $L_{2,3}$  edge and found that the spectrum of  $\text{Mn}^{2+}$  did not match that from the reference compound (MnO). They attributed this discrepancy solely to signal intermixing, disregarding contributions from the difference in coordination [octahedral ( $O_h$ ) versus tetrahedral ( $T_d$ )].

To verify the proposed invariance with coordination, we analyzed the electronic structure of the relevant compounds (Fig. 1) by using hybrid-exchange density functional theory. The adopted Becke three-parameter Lee-Yang-Parr (B3LYP) functional (as implemented in CRYSTAL09 [2,3]) produces band gaps and band widths in agreement with optical spectra [4] and shows quantitative agreement between calculated and experimental formation energies for these Mn oxides [5]. The EEL spectrum is approximated by the projected single-particle density of states, where the  $L_3$  edge corresponds to the on-site transition between the Mn  $2p$  and vacant Mn  $3d$  orbitals. Considering the experimental resolution [1], a Gaussian function of width 0.4 eV is used to broaden the theoretical spectra. The calculated  $L_3$  peaks (left-hand panel in Fig. 1) for  $\text{Mn}^{3+}$  in  $\text{Mn}_3\text{O}_4$  and  $\text{Mn}_2\text{O}_3$  match reasonably well, although the  $\text{Mn}_2\text{O}_3$  feature is broader. The calculated  $\text{Mn}^{2+}$  peaks in  $\text{Mn}_3\text{O}_4$  and MnO also agree except for the presence of a larger shoulder at higher binding energy in  $\text{Mn}_3\text{O}_4$ . This shoulder is rationalized by Tan *et al.* to be due to intermixing, with 22% of the  $\text{Mn}^{3+}$  signal being present on the  $\text{Mn}^{2+}$  site. A simple model for delocalization,  $d_E = 0.5\lambda/\theta_E^{3/4}$  [6,7], suggests a limit of 1.4 Å for the experiment in [1]. This is equal to the distance between the two sites; thus, intermixing is not expected to be pronounced. Additionally, the increase in intensity of the shoulder from the reference  $\text{Mn}^{2+}$  signal in the measured spectra is far greater than the proposed 22% intermixing (Fig. 2 in [1] suggests 50% of the  $\text{Mn}^{3+}$  signal).

An alternative explanation of the  $\text{Mn}_3\text{O}_4$   $L_3$  edge is based on the effect of  $O_h$  versus  $T_d$  coordination on the Mn  $3d$  states. This can be understood by projecting the calculated spectra onto the symmetry distinct  $\text{Mn}^{2+}$   $3d$  states (right-hand panel of Fig. 1).  $\text{MnFe}_2\text{O}_4$  is also included here to provide an additional reference for  $T_d$  coordinated  $\text{Mn}^{2+}$ . It is apparent that in moving from  $O_h$  to  $T_d$  coordination, there is a significant reduction in the intensity of peak *a*. Peak *c* becomes more intense in  $\text{Mn}_3\text{O}_4$ , while also being shifted to a higher binding energy in  $T_d$  coordination. This occurs primarily due to

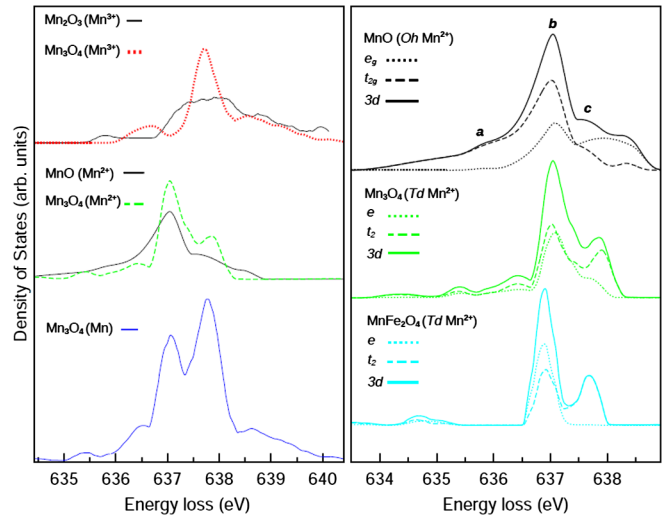


FIG. 1 (color online). Calculated EEL spectra ( $L_3$ ) for  $\text{Mn}^{2+}$  and  $\text{Mn}^{3+}$ . The spectra in the right-hand panel are scaled to have equal peak *b* intensities to aid comparison.

crystal-field splitting, the  $t_2$  ( $T_d$ ) states being at higher binding energy than the  $t_{2g}$  ( $O_h$ ) states. Comparing the measured spectra of MnO [8],  $\text{Mn}_3\text{O}_4$  [1], and  $\text{MnFe}_2\text{O}_4$  [8], similar changes in peaks *a* and *c* are observed. It is notable that the increase in intensity of peak *c* in  $\text{Mn}_3\text{O}_4$  [1] is much larger than that observed in  $\text{MnFe}_2\text{O}_4$  [8], even though both peaks are from  $T_d$ -coordinated  $\text{Mn}^{2+}$ . This is in fact predicted in the calculations where the increase of peak *c* intensity in  $\text{Mn}_3\text{O}_4$  is significantly greater (20%). It is apparent that this is due to the combined contribution of *e* and  $t_2$  states to peak *c* in  $\text{Mn}_3\text{O}_4$ , whereas in  $\text{MnFe}_2\text{O}_4$  only the  $t_2$  states contribute. This confirms that small changes in local environments have a measurable effect on the  $L_3$  edge.

To summarize, the calculations presented here suggest a non-negligible contribution from local coordination to the observed electron energy-loss near edge structure (ELNES), and consequently, these effects cannot be neglected in the interpretation of the site resolved EEL spectra of  $\text{Mn}_3\text{O}_4$ .

This work made use of the high-performance computing facilities of Imperial College London and via membership of the United Kingdom HPC Materials Chemistry Consortium funded by EPSRC (EP/F067496)—of HECToR, the national high-performance computing service of the United Kingdom, which is provided by UoE HPCx Ltd. at the University of Edinburgh, Cray, Inc., and NAG Ltd., and funded by the Office of Science and Technology through High End Computing Programme (EPSRC).

E. A. Ahmad,<sup>1,2,\*</sup> G. Mallia,<sup>1,2</sup> D. Kramer,<sup>3</sup> V. Tileli,<sup>4</sup>  
A. R. Kucernak,<sup>1</sup> and N. M. Harrison<sup>1,2,5</sup>  
<sup>1</sup>Department of Chemistry  
Imperial College London  
South Kensington, London SW7 2AZ, United Kingdom

<sup>2</sup>Thomas Young Centre  
Imperial College London  
South Kensington, London SW7 2AZ, United Kingdom  
<sup>3</sup>Faculty of Engineering and the Environment  
University of Southampton  
University Road, Southampton SO17 1BJ, United Kingdom  
<sup>4</sup>Department of Materials  
Imperial College London  
South Kensington, London SW7 2AZ, United Kingdom  
<sup>5</sup>Daresbury Laboratory  
Daresbury, Warrington, WA4 4AD, United Kingdom

Received 24 November 2011; published 19 June 2012

DOI: [10.1103/PhysRevLett.108.259701](https://doi.org/10.1103/PhysRevLett.108.259701)

PACS numbers: 79.20.Uv, 68.37.Ma, 75.25.Dk

\*[ehsan.ahmad08@imperial.ac.uk](mailto:ehsan.ahmad08@imperial.ac.uk)

[1] H. Tan, S. Turner, E. Yücelen, J. Verbeeck, and G. Van Tendeloo, *Phys. Rev. Lett.* **107**, 107602 (2011).

- [2] A. D. Becke, *J. Chem. Phys.* **98**, 5648 (1993).  
[3] R. Dovesi, V. R. Saunders, C. Roetti, R. Orlando, C. M. Zicovich-Wilson, F. Pascale, B. Civalleri, K. Doll, N. M. Harrison, I. J. Bush *et al.*, *CRYSTAL09 User's Manual* (Università di Torino, Torino, 2010).  
[4] J. Muscat, A. Wander, and N. Harrison, *Chem. Phys. Lett.* **342**, 397 (2001).  
[5] E. A. Ahmad, L. Liborio, D. Kramer, G. Mallia, A. R. Kucernak, and N. M. Harrison, *Phys. Rev. B* **84**, 085137 (2011).  
[6] K. Kimoto, T. Asaka, T. Nagai, M. Saito, Y. Matsui, and K. Ishizuka, *Nature (London)* **450**, 702 (2007).  
[7] M. Haruta, H. Kurata, H. Komatsu, Y. Shimakawa, and S. Isoda, *Phys. Rev. B* **80**, 165123 (2009).  
[8] L. A. J. Garvie and A. J. Craven, *Phys. Chem. Miner.* **21**, 191 (1994).

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