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- 3 We have defined ELNES as electron-energy-loss near-edge structure. Is this correct?

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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 Mn_3O_4 using spatially resolved electron-energy-loss spectroscopy (EELS). They interpreted the EELS spectra of Mn^{2+} and Mn^{3+} sites in terms of the Mn $L_{2,3}$ edge and found that the spectrum of 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 EELS 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 Mn^{3+} in Mn_3O_4 and Mn_2O_3 match reasonably well, although the Mn_2O_3 feature is broader. The calculated Mn^{2+} peaks in Mn_3O_4 and MnO also agree except for the presence of a larger shoulder at higher binding energy in Mn_3O_4 . This shoulder is rationalized by Tan *et al.* to be due to intermixing, with 22% of the Mn^{3+} signal being present on the 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 Mn^{2+} signal in the measured spectra is far greater than the proposed 22% intermixing (Fig. 2 in [1] suggests 50% of the Mn^{3+} signal).

An alternative explanation of the Mn_3O_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 Mn^{2+} $3d$ states (right-hand panel of Fig. 1). MnFe_2O_4 is also included here to provide an additional reference for T_d coordinated 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 Mn_3O_4 , while also being shifted to a higher binding energy in T_d coordination. This occurs primarily due to

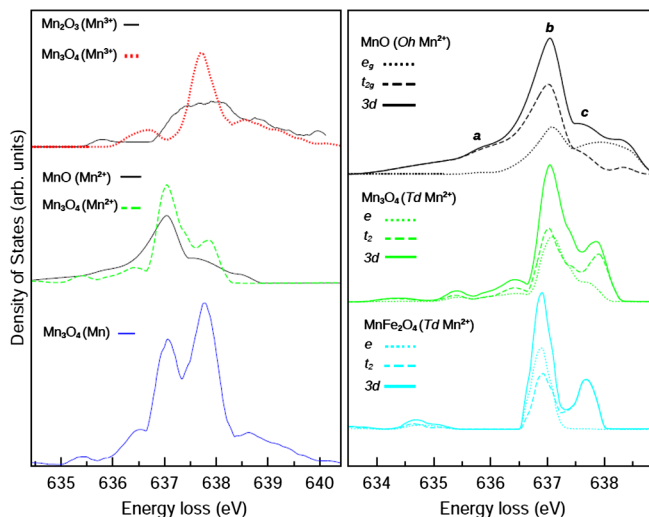


FIG. 1 (color online). Calculated EELS spectra (L_3) for Mn^{2+} and Mn^{3+} . The spectra in the right-hand panel are scaled to have equal peak *b* intensities to aid comparison.

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], Mn_3O_4 [1], and MnFe_2O_4 [8], similar changes in peaks *a* and *c* are observed. It is notable that the increase in intensity of peak *c* in Mn_3O_4 [1] is much larger than that observed in MnFe_2O_4 [8], even though both peaks are from T_d -coordinated Mn^{2+} . This is in fact predicted in the calculations where the increase of peak *c* intensity in Mn_3O_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 Mn_3O_4 , whereas in MnFe_2O_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 EELS spectra of Mn_3O_4 .

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[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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