

Atomic scale understanding of the electronic structure of 5d-3d perovskite oxide heterostructures using STEM-EELS.

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Creating abrupt heterostructures of materials with high spin-orbit coupling (SOC) such as topological insulators, heavy metals, 5d transition metal oxides etc. and ferromagnets such as NiFe, Permalloy, LaMnO₃ etc. can result in high spin to charge conversion, useful for applications in spintronics.^[1] Most of these effects happen only at the interface, but the resolution offered by STEM-EELS provides the ability to study interfacial phenomena and the driving force behind charge to spin conversion. We studied SrIrO₃/La_{0.66}Sr_{0.33}MnO₃ (SIO/LSMO) as a model system to understand at atomic resolution the local electronic structure that produces high spin torque efficiency.

Epitaxial LSMO/SIO bilayers with varying SIO thickness were grown on SrTiO₃ (STO) (0 0 1) substrates by high-pressure reflective high energy electron diffraction (RHEED)-assisted pulsed laser deposition. An atomic resolution HAADF-STEM image is displayed in Figure 1a. A sharp interface is evident from Figure 1(a) with MnO₂ termination in LSMO and SrO termination in SIO. The lattice parameters for various SIO thicknesses were extracted from HAADF-STEM images using Gaussian fitting of each atomic column. The LSMO out-of-plane (OOP) lattice parameter remains unchanged, but the OOP lattice parameter for SIO changes as a function of SIO thickness from 3.97 Å for the 10-unit cell (UC) SIO sample to 4.06 Å for the 30-UC SIO. We note that the SIO OOP lattice parameter (3.97 Å) in the LSMO(50 UC)/SIO(10 UC) is smaller than what has been reported for 30 UC SIO grown on a bulk STO substrate (4.08 Å).

Next, we correlate the electronic structure associated with this puzzling structural evolution by atomic resolution STEM-EELS (Figure 1b). EELS spectral maps were collected using a Gatan Continuum GIF with a K3 direct electron detector. The detector allows atomic mapping of the core-loss edges with high signal to noise ratio even with short dwell times (~2 ms/spectrum). The EELS maps were de-noised using non-negative matrix factorization (NMF) based on Poissonian noise. We observe a sharp LSMO/SIO interface with no Mn/Ir interdiffusion, and a ~-1eV shift of the Mn L-edge in the 10UC SIO sample compared to the 30UC SIO and a reference spectrum^[2] (Figure 1c). These changes in the Mn L-edge point to the strong possibility of a charge transfer from Ir to Mn. We also observe a corresponding change in the O K-edge from the SIO and LSMO layer (Figure 1d). The changes in the first 5eV of the O K-edge from the SIO side reflect changes in the electronic structure of the SIO layer, arising from changes in the Ir-O hybridization. Charge transfer can also be accompanied by orbital reconstruction in the strained SIO layer.^[3,4] Bulk SIO is semimetal with strong spin-orbit coupling (SOC), which is comparable to the crystal field splitting (CFS).^[5] It has been recently reported that CFS can dominate over SOC in strained iridate systems.^[6] Evidence for such an orbital re-construction due to CFS could be seen in O K edge in Figure

1(d). In LSMO(50 UC)/SIO(10 UC) the density of states for Ir-O related levels are broader than that those in LSMO(50 UC)/SIO(30 UC). We believe that due to the dominance of CFS over the SOC, $S=1$ state is stabilized in the LSMO (50 UC)/SIO(10 UC) as seen in nickelate/iridate systems. [4] We hypothesize that the changes in O K-edge spectra of SIO are due to a combination of charge transfer and orbital reconstruction (Figure 2). We note that for LSMO(50 UC)/SIO(30 UC), where the charge transfer is negligible, there is no orbital reconstruction in Ir 5d levels.

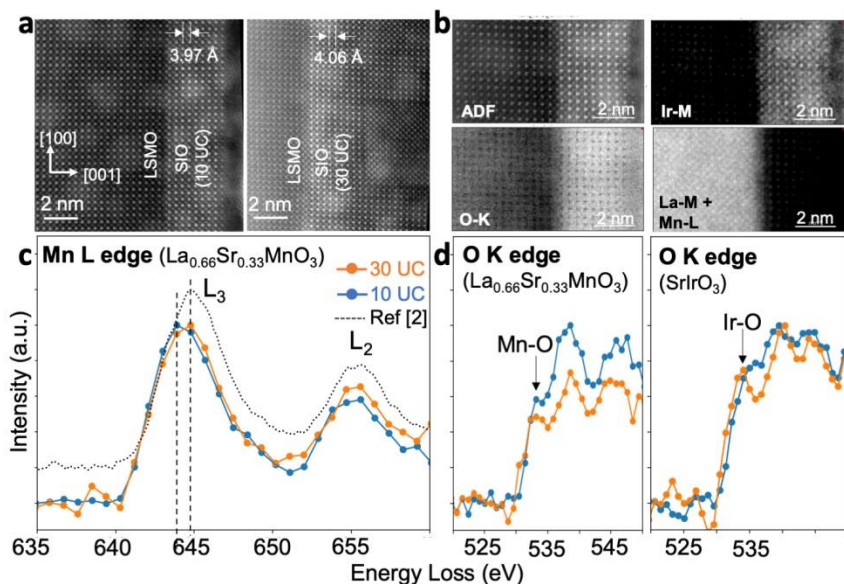


Figure 1. Figure 1: a) HAADF-STEM images of SIO/LSMO bilayers with 10UC and 30 UC SIO thickness. Overlaid are the OOP plane spacing in SIO extracted from lattice fitting. b) Atomic resolution STEM-EELS maps of LSMO/SIO displaying a sharp interface and no Mn/Ir interdiffusion. c) Average Mn L edge spectra extracted from the LSMO side of different LSMO/SIO heterostructures with a reference spectrum.[2] d) Average O K-edge extracted from LSMO and SIO sides showing different electronic structures depending on SIO thickness.

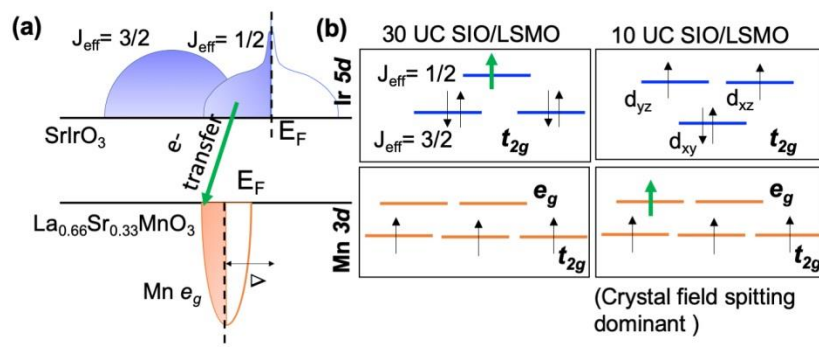


Figure 2. Figure 2: a) The electronic arrangement of LSMO/SIO showing the electron charge transfer from Ir⁴⁺ (SrIrO₃) to Mn⁴⁺ (La_{0.7}Sr_{0.3}MnO₃) b) Orbital reconstruction of Mn 3d and Ir 5d levels for LSMO (50 UC)/SIO(10 UC) after the electron transfer. No electron transfer occurs for LSMO (50 UC)/SIO(30 UC).

References

- [1] W. Han, Y. Otani, S. Maekawa, *npj Quantum Mater.* **2018**, 3, 1.
- [2] P. Ewels, T. Sikora, V. Serin, C. P. Ewels, L. Lajaunie, *Microsc. Microanal.* **2016**, 22, 717.
- [3] D. Yi, J. Liu, S.-L. Hsu, L. Zhang, Y. Choi, J.-W. Kim, Z. Chen, J. D. Clarkson, C. R. Serrao, E. Arenholz, P. J. Ryan, H. Xu, R. J. Birgeneau, R. Ramesh, *Proc. Natl. Acad. Sci.* **2016**, 113, 6397 LP.
- [4] X. Liu, M. Kotiuga, H.-S. Kim, Y. Choi, Q. Zhang, Y. Cao, M. Kareev, F. Wen, B. Pal, J. W. Freeland, *Proc. Natl. Acad. Sci.* **2019**, 116, 19863.
- [5] M. A. Zeb, H.-Y. Kee, *Phys. Rev. B* **2012**, 86, 85149.
- [6] X. Liu, V. M. Katukuri, L. Hozoi, W.-G. Yin, M. P. M. Dean, M. H. Upton, J. Kim, D. Casa, A. Said, T. Gog, *Phys. Rev. Lett.* **2012**, 109, 157401.
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