Surface Energies of LaMnO$_3$ High-Index Surfaces Obtained from Density-Functional Theory
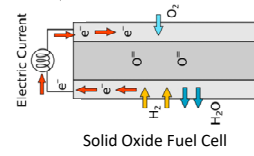
Yves A. Mantz[1] and Yueh-Lin Lee[2,3]

[1]US Department of Energy, National Energy Technology Laboratory, Morgantown WV; [2]US Department of Energy, National Energy Technology Laboratory, Pittsburgh PA; [3]NETL Support Contractor, Pittsburgh PA

Research & Innovation Center

Introduction

- Study of LaMnO$_3$ (LM) surfaces is important
  - In certain solid oxide fuel cells, the reduction of oxygen on Sr-doped LM is critical to cell performance.
  - To understand the reduction process better, the key Sr-doped LM surfaces present under cell operating conditions need to be identified.
  - To identify these surfaces, the energetics of cubic LM surfaces are appropriate to examine.
- In previous theoretical studies,[1–4] the surface energies of the cubic LM low-index surfaces, (001), (011), and (111), were determined (see right).
- Building upon this work, the first six cubic LM low-index surfaces are examined here for the first time.[5]

Solid Oxide Fuel Cell
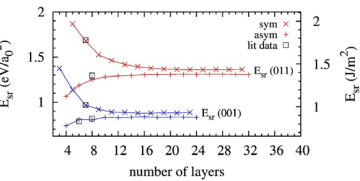
Relaxed surface energies E_{sr} versus model thickness using two different model types from ref 4 compared to literature data.[1–3]

Computational Approach

- Computations are performed at the level of spin-unrestricted density-functional theory (PW91 functional, 600 eV cutoff, PAW pseudopotentials) using the VASP software package,[6] as in ref 4.
- The (210), (211), (221), (310), (311), (320) surfaces are examined.
- Each surface is described by one of the following sequences of layers. Thus, two surface terminations of a surface are possible.
  - LaO – MnO$_2$ – LaO – MnO$_2$ –…
  - LaMnO – O$_2$ – LaMnO – O$_2$ – …
  - LaO$_3$ – Mn – LaO$_3$ – Mn – …
- The surfaces are modeled using asymmetric surface models (having different surface terminations on the top and bottom of the slab). Note, dipole-dipole coupling between periodic images is weak.
- Unrelaxed and relaxed surface energies E_{su} and E_{sr} are computed versus surface model thickness using the following equation:[4]

$$E_s = \frac{1}{2A}\left(E_{slab} - nE^{bulk}\right)$$

E_{slab}: energy of unrelaxed or relaxed slab
n: formula units (f.u.'s) in a slab
E^{bulk}: energy of bulk LM per f.u.
A: area of one side of a slab

- E^{bulk} is determined using a linear-fit procedure[7–9] to obtain a flat E_{su} or E_{sr} curve at a model thickness $N \geq N^*$ layers, as illustrated below for the E_{su} curve of the (211) surface, where $N^* = 10$.
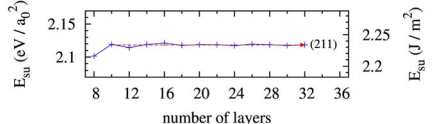

- **Twelve different E^{bulk} values are determined**, one for the unrelaxed and one for the relaxed surface models of each surface examined in this work.

Results for (210), (211), (221), and (320) Surfaces
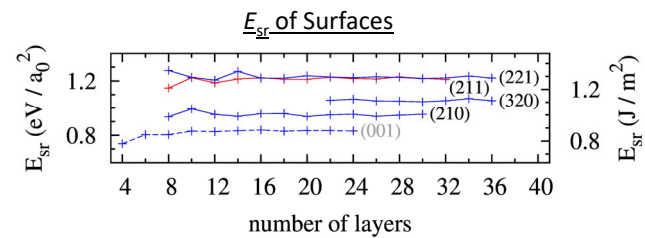
E_{sr} of Surfaces

- The E_{sr} of the (210), (211), (221), and (320) surfaces are 0.95, 1.22, 1.23, and 1.06 eV/a_0^2, respectively, more than the E_{sr} of (001), 0.83 eV/a_0^2, but less than the E_{sr} of (011) and (111), 1.31 and 1.34 eV/a_0^2, respectively (given in ref 4).
- The E_{su} of the surfaces are significantly larger than the E_{sr}.

Structures of Surfaces
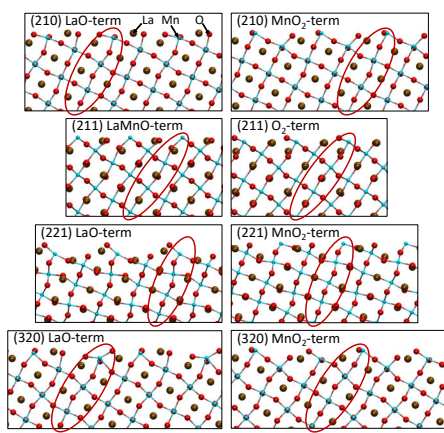
- Helping to explain the relatively small E_{sr}, the surface terminations of the surfaces are seen to exhibit a rotational relaxation of the MnO$_6$ or oxygen octahedra (e.g., the red circled regions at right), leading to distorted surfaces.
- This relaxation is believed to occur because a different phase of LM is stable at the temperature of the computations, 0 K, and it is seen to exhibit a rotational relaxation.[10–12]

- Note, the surface terminations are sitting atop distorted bulk structures, but the above structures are accurate, based on additional computations done.
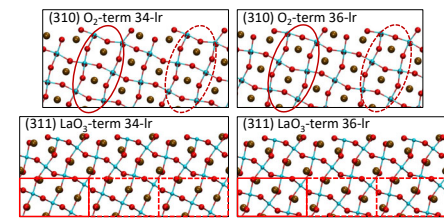
Results for (310) and (311) Surfaces

E_{sr} of Surfaces
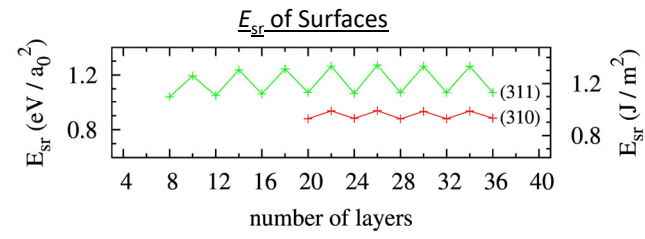
- The E_{sr} curves of the (310) and (311) surfaces are seen to exhibit an unusual triangular form, with minima at $4x = 20$, 24, 28, 32, and 36 layers and maxima at $4x + 2 = 22$, 26, 30, and 34 layers. This form needs to be explained.

Results for (310) and (311) Surfaces (Cntd)

Explanation for Triangular Curves

- The triangular form is due to different structures of the surface models with $4x$ and $4x + 2$ layers, seen by comparing red circled or boxed regions at right.
- The different structures are explained by a structural transformation or phase change in the surface models of the surfaces, as shown at right. If a phase change is seen, then different structures are possible.
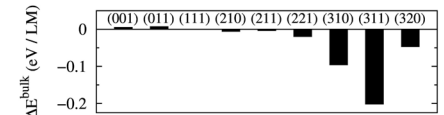
ΔE^{bulk} of a surface is the difference of E^{bulk} values obtained for the relaxed and unrelaxed models of a surface.

Conclusions

- The (210), (211), (221), and (320) surfaces are relatively stable. Helping to explain this result, the surface terminations of the surfaces are seen to exhibit a rotational relaxation of the oxygen octahedra.
  - This rotational relaxation is the first example of a rotational relaxation seen at the surfaces of a cubic perovskite oxide <u>not</u> undergoing a phase change to an antiferrodistortive phase.
- The relaxed (310) and (311) surfaces are difficult to characterize due to a phase change in the surface models of the surfaces.
  - This result indicates a phase change in the surface models of other surfaces may occur.
  - Steps to model these surfaces are suggested (given in ref 5).

Acknowledgment

References and Disclaimer

[1] RA Evarestov et al, Phys Rev B 72, 214411 (2005) [2] YA Mastrikov et al, Surf Sci 603, 326 (2009) [3] YM Choi et al, Chem Mater 19, 1690 (2007) [4] YA Mantz, Surf Sci 695, 121500 (2020) [5] YA Mantz and YL Lee, submitted to J Phys Chem C [6] https://www.vasp.at [7] V Fiorentini and M Methfessel, J Phys: Condens Matter 8, 6525 (1996) [8] JC Boettger et al, J Phys: Condens Matter 10, 893 (1998) [9] V Fiorentini and M Methfessel, J Phys: Condens Matter 10, 895 (1998) [10] F Bottin et al, Phys Rev B 68, 035418 (2003) [11] H Chen et al, J Phys: Condens Matter 26, 395002 (2014) [12] H Chen et al, Mater Chem Phys 174, 195 (2016)

U.S. DEPARTMENT OF ENERGY

Science & Engineering To Power Our Future