Surface Energies of LaMnO₃ High-Index Surfaces Obtained from Density-Functional Theory

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Introduction

- Study of LaMnO₃ (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, 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.

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, 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–MnO₂–LaO–MnO₂–...
  - LaMnO₃–O₂–LaMnO₃–O₂–...
  - LaO₃–Mn–LaO₂–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 $E_u$ and $E_r$ are computed versus surface model thickness using the following equation:

$$ E_s = \frac{1}{2A} (E_{slab} - nE_{bulk}) $$

$E_{slab}$: energy of unrelaxed or relaxed slab
$E_{bulk}$: bulk of a surface is the difference of bulk values obtained for the relaxed and unrelaxed models of a surface.

$E_u$ is determined using a linear-fit procedure, to obtain a flat $E_u$ curve at a model thickness $N ≥ N^*$ layers, as illustrated below for the $E_u$ 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

- The $E_u$ of the (210), (211), (221), and (320) surfaces are 0.95, 1.22, 1.23, and 1.06 eV/Å², respectively, more than the $E_u$ of (001), 0.83 eV/Å², but less than the $E_u$ of (011) and (111), 1.31 and 1.34 eV/Å², respectively (given in ref 4).
- The $E_u$ of the surfaces are significantly larger than the $E_u$ of the (311) surfaces.
- Helping to explain the relatively small $E_r$, the surface terminations of the surfaces are seen to exhibit a rotational relaxation of the MnO₃ 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.

Results for (310) and (311) Surfaces

- The $E_r$ of the (310) and (311) surfaces are seen to exhibit an unusual triangular form, with minima at 4x + 2 = 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 (Cndtd)

- 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.

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 not 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).

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References and Disclaimer

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