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Simulation of the surface structure of lithium manganese oxide spinel

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Simulations of the surface structure of low-index surfaces of LiMn_2O_4 , a candidate Li-ion battery electrode material, have been performed within the GGA+ U approximation, using the VASP code. Surfaces of (001), (110), and (111) orientation were considered, with at least two terminations treated in each case. A slab geometry was employed, with termination-layer vacancies introduced to remove the bulk dipole moment, while maintaining ideal stoichiometry. To complement static-structure relaxation calculations, molecular dynamics simulations were performed to explore the phase space of possible surface reconstructions. A reconstruction is predicted for the Mn-terminated (111) surface, in which the top layers mix in stoichiometric proportions to form an LMO termination layer with square-planar-coordinated Mn. Average surface Mn oxidation states are reduced, relative to the bulk, for all surfaces considered, as a consequence of the lower energy cost of Jahn-Teller distortion at the surface. Threefold-coordinated surface Mn, found for two terminations, is divalent, which may enhance vulnerability to dissolution. The Li-terminated (001) surface is lowest in energy, consistent with previous classical-potential simulations for MgAl_2O_4 that showed the Mg-terminated (001) surface to be lowest in energy.

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I. I. INTRODUCTION

Lithium manganese oxide spinel LiMn_2O_4 (LMO) is a candidate electrode material for lithium-ion batteries¹. At room temperature, LMO adopts the same cubic crystal structure as the prototype spinel, MgAl_2O_4 , with symmetry $Fd\bar{3}m$. As for many ternary oxides, however, the surface atomic structure is poorly known for LMO. Characterization of the surface and interfacial structures of LMO would be a step towards understanding its chemical and electrochemical reactions. The significance of surface and interface properties is further accentuated by the focus on nanostructured electrodes², which shorten Li diffusion paths.

Among direct spinel-structured surfaces, that of magnesium aluminum oxide has perhaps received the most theoretical attention. Atomic-scale simulations were performed of low index surfaces of MgAl_2O_4 , based on semi-empirical

interatomic potentials^{3,4}. Cation terminations for the low energy orientation, (001), have been simulated with density functional theory⁵. The (111) orientation was found to exhibit the most extensive atomic rearrangements at the surface.

Compared to MgAl_2O_4 , LMO has the extra complications of Mn disproportionation and Jahn-Teller activity of the trivalent ions. These features are amenable to simulation at the GGA+ U level of density functional theory^{6,7}. Previous first-principles simulations of the surface structure of LiMn_2O_4 , however, appear limited to a recent investigation of the (001) surface⁸.

In this article, we present simulations of essentially all low-index surfaces of LiMn_2O_4 using the GGA+ U method, as implemented in the VASP code^{9–11} with PAW (projector-augmented wave) pseudopotentials. This work is intended to provide insight into surface atomic structure and atomic structure data that may be employed in future simulations of dissolution of lithium manganate spinel in acid^{12,13}. The atomic structure input data may also provides input for simulations of lithium manganate interfaces, for example with protective coatings¹⁴ or electrolyte.

A periodically repeated slab geometry is convenient for surface calculations. Since the low-index orientations are polar (Tasker type III¹⁵), an unphysical dipole moment perpendicular to the slab occurs unless surface defects (e.g., vacancies), surface electronic states, or other reconstructions, are introduced¹⁶. To reduce the computational burden, only compositions with ideal stoichiometry (canonical ensemble) are considered in this work. Ideal stoichiometry is maintained by transferring atoms from one surface of the slab to the opposite surface¹⁷.

Given the variety of terminations that are possible, the identification of common features of lithium manganate surfaces is of particular interest. In this work, we consider all low index surface terminations derived from a symmetry plane (so that the slab may be constructed with essentially identical top and bottom surfaces), and, additionally, the oxygen terminated (111) surface, which is asymmetrical. This set of seven terminations [two (001), two (110) and three (111)], are sufficient to reveal some pervasive features of lithium manganate spinel free surfaces, including the reduced average oxidation state of Mn ions near the surface, the presence of Mn coordination numbers that range from three to five (in contrast to octahedral coordination in the bulk) and the absence of non-bridging (singly coordinated) oxygen at flat surfaces.

In recent years, first-principles simulations of several binary oxide surfaces, such as MnO ¹⁸, have been performed as a function of oxygen partial pressure, within the grand canonical ensemble. In such simulations, a small number of candidate reconstructions is identified, and the surface free energy evaluated for each. A recent grand canonical ensemble surface simulation has been performed for the ternary, LiCoO_2 ¹⁹. For many ternaries, however, the large

number and complexity of candidate reconstructions may make this approach prohibitive, and the present work is performed within the canonical ensemble. In this work, instead of attempting to select relevant candidate surface structures, we employ first principles molecular dynamics to explore the phase space of possible reconstructions. In the case of the Mn-terminated (111) surface, an atomic rearrangement and ordering was found in which the three components are mixed to form a composite stoichiometric surface layer with square planar coordination of Mn ions in the surface plane. Direct experimental tests of this prediction are not presently available. The prediction suggests, however, that the bulk-terminated surface is highly unstable, and that extensive atomic rearrangements of (111) surfaces are likely.

In the analysis presented in the following sections, we focus on surface Mn oxidation states and coordination numbers, which are relevant to the surface reactions of lithium manganate, to be addressed in future work. We consider here only pristine surfaces, although hydroxylation is a ubiquitous feature of real surfaces²⁰. Despite the difficulty of measurements, pristine surfaces are an important benchmark for simulation.

II. II. SLAB REPRESENTATION OF LITHIUM MANGANATE SURFACES

We outline here the construction of bulk-terminated slabs, which are employed as (pre-relaxation) input atomic position data in the VASP calculations. The degrees of freedom of the slab include (a) the surface orientation, (b) the termination plane, (c) the size of the slab unit cell parallel and perpendicular to the surface (slab thickness), and (d) the configuration of surface vacancies, introduced to cancel the surface dipole moment^{16,17}, which would otherwise result in energy divergences for Tasker type III surfaces in the limit of thick slabs. We consider the low-index surface orientations (001), (110), and (111). Specification of the degrees of freedom (b)-(d) is described in the following subsections.

A. Slab layer sequences

All surface terminations obtained from symmetrical cleavage planes for low index surfaces are considered in this work. In addition, asymmetrical O-terminated surfaces for the (111) surface are addressed. Altogether, two (001) terminations, two (110) terminations, and three (111) terminations are considered. For slab terminations associated with symmetrical cleavage planes, the macroscopic electrostatic dipole moment is automatically canceled when the half of the atoms in the bulk termination layer are assigned to the top and half to the bottom layer of the slab, which

results in a termination layer vacancy concentration $C_v = 1/2$. For slabs derived from asymmetric cleavage planes, a different vacancy concentration is required to cancel the macroscopic dipole moment¹⁷.

The underlying layer sequences for low-index orientations, from which the various terminations are derived, are reviewed in the following subsections.

1. (111) surface

(111) atomic layers in bulk LiMn_2O_4 follow the sequence $(\dots\text{M}_3;\text{O}_4;\text{L,M,L};\text{O}_4;\text{M}_3\dots)$, where the relative layer atomic density is indicated by the subscripts; for example, the M_3 layers have 3/4 as many atoms, per unit layer area, as the O_4 layers. M occupies octahedral sites in the M_3 layers. Since the L,M,L triple cation layers (with tetrahedral L and octahedral M) are closely spaced, we regard them as sublayers of a single composite layer. [Semicolons separate distinct layers and commas separate sublayers of the LML composite layer].

Two symmetry planes occur in the (111) layer sequence, both of which correspond to Mn-bearing termination surfaces. The cleavage plane in one case is at a pure Mn layer sandwiched between oxygen layers, and in the other is at the center of a L,M,L composite layer. The layer sequence for the first such termination (at ideal stoichiometry) is

$$((1 - C_v)\text{M}_3; \text{O}_4; \text{L,M,L}; \text{O}_4; \text{M}_3; \text{O}_4, \text{L,M,L}; \dots \text{O}_4; C_v\text{M}_3). \quad (1)$$

The (stoichiometry-conserving) termination layer compositions includes the factors $1 - C_v$ and C_v , on the top and bottom of the slab, respectively, where $C_v = 1/2$ ($1 - C_v = 1/2$) are the vacancy concentration at the top (bottom) of the slab.

The resultant sequence may be regarded as a stacking of stoichiometric, zero-dipole-moment $(1/2\text{M}_3;\text{O}_4;\text{L,M,L};\text{O}_4;1/2\text{M}_3)$ units perpendicular to the plane of the surface. The slab obtained by the stacking of such units can be viewed as a minimally reconstructed surface: atoms are in bulk terminated sites, with a configuration of vacancies in termination layer. More general reconstructions, that would involve, e.g., additional surface vacancies are not considered in the present work.

As mentioned above (item (c)), the size of the unit cell parallel and perpendicular to the surface e.g., the number of such stacking units perpendicular, n_{perp} , and parallel, n_{par} , to the surface, must be specified to fix the number of degrees of freedom for the slab. The minimal value of n_{par} is 2 in this case, to give integral numbers of atoms in the (top and bottom) terminating layers of the periodic unit cell of the slab.

The sequence of layers for cleavage at the (L,M,L) layer is

$$(1/2\text{M,L;O}_4; \text{M}_3; \text{O}_4; \text{L,M,L}; \dots, \text{M}_3; \text{O}_4; \text{L}, 1/2\text{M}), \quad (2)$$

and the corresponding stoichiometric stacking unit is $(1/2\text{M,L;O}_4; \text{M}_3; \text{O}_4; \text{L}, 1/2\text{M})$.

A stoichiometric slab terminated at the oxygen layer has the sequence

$$(1 - C_v)\text{O}_4; \text{L,M,L;O}_4; \text{M}_3; \text{O}_4; \text{L,M,L}; \dots \text{O}_4; \dots \text{M}_3; C_v\text{O}_4. \quad (3)$$

Since cleavage is at an asymmetrical plane in this case, the dipole-moment canceling value¹⁷ of C_v deviates from one half. If we assume (bulk average) charges of -2, +3.5, and +1 on oxygen ions, Mn ions, and Li ions, respectively, we obtain $C_v = 0.3125$. Therefore $C_v \approx 5/8$ and three of eight oxygen sites are left vacant in the termination layer above a Mn layer, and five oxygen sites are vacant at the opposite termination layer.

The initial atomic coordinates for a bulk-terminated slab can be fixed by specifying the termination, the slab size parameters n_{perp} and n_{par} , and the vacancy arrangement of the terminating layers. For (111) slabs, we have selected $n_{\text{perp}} = 3$ and $n_{\text{par}} = 2$. Since the stacking unit given above contains two LiMn_2O_4 formula units, the periodic unit of each such slab contains $2 \times 3 \times 2 = 12$ formula units, or 84 atoms. The selected cell unit vectors A_1 and A_2 parallel to the surface and the termination layer vacancy configuration for the (M;O) termination, are illustrated in Fig. 1. The initial configuration of vacancies is chosen so as to minimize the deficit of M-O bonds at the surface¹⁹; this choice is not necessarily unique, however.

2. (001) surface

The layer sequence for a slab with (001) orientation may be regarded as an alternation between M_4O_8 and L_2 layers, and each type of layer is a possible symmetric cleavage plane. The layer sequence for the MO termination is thus

$$1/2(\text{M}_4\text{O}_8); \text{L}_2; \text{M}_4\text{O}_8; \text{L}_2; \dots, 1/2(\text{M}_4\text{O}_8) \quad (4)$$

and the stoichiometric stacking unit is $1/2(\text{M}_4\text{O}_8); \text{L}_2; 1/2(\text{M}_4\text{O}_8)$. The sequence for the L termination is

$$1/2(\text{L})_2; \text{M}_4\text{O}_8; \text{L}_2; \dots, \text{M}_4\text{O}_8; 1/2(\text{L})_2. \quad (5)$$

The termination-layer unit cell employed for the MO termination is illustrated in Fig. 2. To test the convergence of the calculations with slab thickness, calculations were performed for two slab thicknesses, for the MO termination, with $n_{\text{perp}} = 4$ and 8, which correspond to 56 and 112 atom unit cells, respectively. The larger of these corresponds essentially to the cell size employed by Ouyang, et al.⁸.

3. (110) surface

An alternation occurs between LMO_2 and MO_2 layers in slabs with (110) orientation, each of which presents a symmetric cleavage plane. Thus the sequence for the MO termination is

$$1/2(\text{MO}_2), \text{LMO}_2, \dots 1/2(\text{MO}_2), \quad (6)$$

and the stoichiometric stacking unit is $1/2(\text{MO}_2); \text{LMO}_2; 1/2(\text{MO}_2)$. The termination-layer unit cell for the MO termination is illustrated in Fig. 3. (110) surface calculations were performed for 84-atom unit-cell slabs.

III. METHOD OF CALCULATION

The GGA+ U approximation was employed in this work, as implemented in the VASP code, version 4.6^{9–11}, with PW91 exchange-correlation potential²¹, and effective Coulomb interaction parameter $U_{\text{eff}} = 4.84 \text{ eV}$ ⁶. The Hellmann-Feynman forces obtained from the Kohn-Sham orbitals are employed either in atomic relaxation calculations by the conjugate gradient method, or in first principles molecular dynamics simulations.

Slab unit cell atomic arrangements were constructed, as outlined in the previous section, for three low index orientations of LiMn_2O_4 , with initial atomic coordinates taken from bulk calculations. Lattice basis vectors parallel to slab layers were chosen to be consistent with (calculated) bulk cubic crystal lattice parameters¹³. Bulk LiMn_2O_4 is cubic at room temperature, although symmetry-lowering phase transitions occur at lower temperatures²². Adjacent slabs are separated in the perpendicular direction by a 1 nm vacuum layer. For simplicity, ferromagnetic spin ordering is considered. The relaxation calculations were performed with the 500-eV high-precision setting. In most of the calculations, a single k-point gave satisfactory convergence, for present purposes, although some tests were done with larger k-point sets. The first-principles molecular dynamics simulations for the (111) oriented slab were performed at the low-precision setting (energy cutoff 300 eV) with a single k-point. Since Mn ions are invariably in a high-spin state, the magnetic moment reveals the oxidation state.

The initial relaxation calculation for each slab was performed with conjugate gradients. First principles molecular dynamics thermalization simulations at 300K were then performed for a simulation time of the order of one picosecond on the relaxed slabs to minimize the likelihood of trapping in a local energy minimum configuration. Conjugate gradient relaxation was then alternated with first principles molecular dynamics simulation until a relatively low energy plateau was reached, and the atomic structure was reasonably well converged; structural convergence may require a long simulation time. In the case of the Mn-terminated (111) surface, which exhibited the most extensive

atomic rearrangement, the MD simulation was continued for a total time of about ten picoseconds. For the (001) and (110) surfaces, the thermalization/conjugate gradient steps did not appreciably lower the energy, or change the structure, from that obtained in the initial relaxation.

IV. IV. RESULTS

A. Cleavage energy

The cleavage energy (energy difference between the slab with atoms in (unrelaxed) bulk-terminated sites, and the perfect crystal energy, normalized to the surface area) is a measure of the relative stability of different surface orientations and terminations. Cleavage energies for the seven terminations under consideration are plotted in Fig. 4. The relative magnitude of the various energies can be rationalized to some extent by counting broken bonds. For example, the vastly larger energy for cleavage at the (111) M layer than at the (111) L,M,L composite layer would be expected since the former involves breaking 12 M-O bonds (for the chosen layer unit cell) as compared to 6 M-O and 4L-O bonds for the latter. In general, the (111) terminations, whose layers are either pure cation or pure anion, and thus have no intra-layer bonding, show the most extensive rearrangements when allowed to relax, as discussed in the following subsection.

B. Surface relaxation

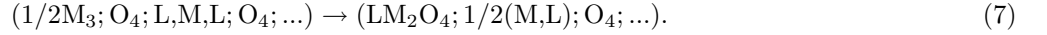
The (111) surfaces show the most extensive atomic rearrangements of the low index surfaces. The results are presented in the following sections.

1. Mn-terminated (111) surface reconstruction

A snapshot of the final reconstructed atomic configuration of the Mn-terminated (111) surface is shown in Fig. 5, in which the atomic positions are projected onto a plane perpendicular to the layers. (For better visualization, the plotted volume includes eight times the number of atoms in the computational cell, 672 atoms, so that the box that encloses the atoms in the figure is roughly cubic.) Atoms in ideally flat atomic layers would fall on a straight line in this projection. Owing to the Jahn-Teller distortion, however, a similar projection of a slab with bulk-terminated atomic coordinates shows some layer rumpling, particularly the oxygen layers (Fig. 6).

Whereas bulk (111) layers are of three types, M, O, and L,M,L, (Fig. 6), the reconstructed slab shows a termination layer (LMO) that mixes all three components. The reconstruction may be viewed as a migration of the oxygen atoms in the second layer toward the surface to improve bonding with the terminating M layer; L atoms from (the top sublayer of) the LML layer are then drawn towards the surface in the wake of the oxygen atoms to help maintain electrostatic balance.

The atomic rearrangement during reconstruction can be described schematically by the reaction



thus, in the reconstructed surface, a mixed LMO layer of stoichiometric composition is superposed on a slab with the (L,M,L) termination (cf. sequence (2)). We note that this LMO layer bears a negative charge, since Mn atoms in this layer are predominantly trivalent, as described below.

A planar projection of the reconstructed LMO termination layer is shown in Fig. 7. The Mn ions are coordinated in distorted square planar complexes, with mutual edge and corner sharing. The Li ions are three-fold coordinated. The square-planar configuration is favorable for trivalent Mn from a crystal-field viewpoint since the $e_g(3z^2 - r^2)$ orbital lobes pointing into the vacuum is unconstrained by a ligand. The lobes pointing into the slab, however, are constrained by the adjacent M,L layer atoms, which may be responsible for the relatively large spacing (about 0.2 nm) of the LMO and M,L layer, relative to interlayer spacings in the interior of the slab (cf. Figs. 5 and 8, discussed below). Thus, with the observed separation of the LMO and M,L layers, the closest cation-cation separation is of order 0.28 nm, consistent with cation-cation separations in the bulk.

2. Other (111) terminations

The driving force for reconstruction of other (111) terminations is lower than that for the Mn-layer termination, and only for the Mn termination are intermixed LMO layers such as those shown in Fig. 7 predicted. Some features of the reconstructed Mn-terminated (111) surface are nevertheless also observed in the other terminations. For the surface derived from cleavage at the (L,M,L) layer, the surface Li ions are coordinated only to three oxygen ions. These Li ions are found to relax toward the adjacent oxygen plane, to form almost planar 3-fold-coordinated Li-O complexes, reminiscent of Fig. 7. In the case of the O-terminated (111) surface, some of the sub-surface Mn occur in 4-fold coordinated configurations. Unlike in the Mn-terminated surface, however, these complexes are not square planar, but highly distorted tetrahedra. In both cases, however, the 4-coordinated Mn are trivalent.

C. Surface coordination numbers

The extensive atomic rearrangement of the Mn-terminated (111) surface is driven in part by the low surface Mn ion coordination number of three. The Mn coordination number of the reconstructed surface is raised to four, and that of Li to three.

Despite the high energy associated with three-fold coordinated Mn, coordination numbers of three are found in two other interfaces, the MO-terminated (110) surface and the (M,L)-terminated (111) surface. Despite the relatively high energy of such configurations, the simulated room temperature thermalization of these surfaces by molecular dynamics did not yield any increase the Mn coordination. The under-coordinated ionic environments for the various surfaces simulated in this work are listed in Table I.

D. Oxidation states

An consequence of the lowered coordination is reduced average Mn oxidation states of near-surface Mn ions, relative to the bulk, for all orientations and terminations simulated in this work. Most surface Mn ions with four or five-fold coordination are predicted to be trivalent, and, for three-fold coordinated Mn, divalent states are also found. The results for the seven different orientation/termination combinations treated are listed in Table II.

E. Surface energy

The surface energy, γ , is defined as the difference between bulk and (relaxed) slab energy, per unit surface area. Results for the surface energies calculated in this work are shown in Table III, along with the ratio of the surface energy to cleavage energy (cf. Fig. 4).

The lowest energy is found for the Li-terminated (001) surface, which is derived from a cleavage that breaks a relatively small number of bonds. The low energy of this surface is consistent with the low energy for the Mg terminated MgAl_2O_4 surface⁴ of the prototype spinel. Another relatively low γ surface is the (M,L)-terminated (111) surface, which also is created by breaking a relatively small number of bonds. The LMO-terminated (111) surface, which has the most extensive relaxation, has the lowest ratio of surface to cleavage energy. With both M-O and L-O bonding in the termination plane, the LMO terminated-(110) interface shows the lowest relaxation (and highest ratio of surface to cleavage energy).

The absolute values of γ predicted in this work are somewhat less than those predicted for the corresponding

surfaces of MgAl_2O_4 ⁴. The magnitude of the surface energies calculated in this work, however, are closer to those predicted for $\text{MnO}(001)$ and (110) ²³. The surface energy for the MnO terminated (001) surface is higher than the value of 0.35 J/m^2 obtained by Ouyang et al.⁸. This discrepancy may be primarily due to different values of C_v . The use of $C_v = 1/2$ rather than 0^8 increases the coordination deficit at the surface and therefore the surface energy.

V. V. DISCUSSION

A. Reduced oxidation state of surface Mn

The reduced states of Mn ions near the surface are mostly a consequence of the lower energy cost of Jahn-Teller distortion in the under-coordinated environment near the surface. This is particularly the case for square-planar coordination in the reconstructed (111) surface, and to a lesser extent for five-fold coordinated surface complexes. The energy cost of the Jahn-Teller distortion associated with elongating the O-O separation along polar axes of Mn-O_6 octahedra in the bulk, which stabilize the Mn e_g electron of the trivalent ion, is eliminated in the square planar coordination, since polar-axis oxygens are not present.

Since all Mn ions in the the reconstructed stoichiometric LMO layer of the reconstructed (111) surface (Fig. 5) are trivalent (rather than, say, half trivalent and half tetravalent, as in the bulk), the LMO layer is negatively charged. The surface LMO layer is therefore electrostatically attracted to the positively-charged interior of the slab, although cation-cation repulsion keeps the LMO layer separated from the M,L layer by about 0.2 nm (Fig. 5).

Non-square-planar fourfold-coordinated Mn also occurs (for example, the $(001)\text{MO}$ termination and the (110) LMO termination). Tetrahedrally coordinated Mn tends to favor the divalent oxidation state²⁴, based on crystal field splitting. Our results, however, show Mn in the trivalent rather than divalent states for the four-fold coordinated complexes at the $(001)\text{MO}$ and $(110)\text{LMO}$ surfaces. The O-ion cages surrounding the 4-coordinated Mn are severely distorted from ideal tetrahedra, so additional splitting may occur, which may help stabilize the trivalent state.

Although four-fold coordinated Mn in the divalent state was not found, divalent 3-coordinated Mn was observed (at the $(110)\text{MO}$ and the $(111)\text{M,L}$ surfaces). While divalent Mn is absent from bulk LiMn_2O_4 , its presence at the surface might facilitate dissolution, since the disproportionation reaction¹² $2\text{Mn}^{3+} \rightarrow \text{Mn}^{4+} + \text{Mn}^{2+}$ would not be required (trivalent Mn dissolves only to a negligible extent). An experimental test of the prediction of divalent Mn ions at the surface of LiMn_2O_4 would be useful.

As indicated, 3-coordinated Mn ions were found at the lowest energy $(110)\text{MO}$ surface. We mention, however,

that an interface with a slightly higher energy occurs if a different initial configuration of surface vacancies than in Figure 3 is adopted. The higher energy surface would feature (trivalent) 4-coordinated Mn, but at the cost of having non-bridging oxygen. This suggests that non-bridging oxygen may be a more unfavorable feature than 3-coordinated Mn.

B. Mn-terminated (111) surface reconstruction

X-ray reflectometry (XRR) measurements have been made on LiMn_2O_4 films with different orientations²⁵). The XRR spectra for the (111) orientation required a more elaborate model, with an additional “impurity” layer, than the other low index orientations, to reproduce the data, either for the as-grown films, or after soaking with electrolyte. Our calculations showed an extensive rearrangement, relative to the bulk-terminated surface, for the Mn-termination, but less pronounced rearrangements for the other terminations considered [(L,M) and O terminations]. It is tempting to associate the simulated Mn-terminated (111) surface reconstruction with the behavior observed in XRR, however, the Mn-termination is not the one with the lowest surface energy (Table III).

Because of its relatively high energy, the significance of the reconstructed Mn-terminated (111) surface remains in question. The large decrease in the Mn-terminated (111) surface energy for the reconstructed surface, relative to the cleavage energy, indicates that the driving force for reconstruction of such a surface would be strong. That the reconstruction can be accomplished by a rearrangement that results in square-planar Mn coordination, with the three components mixed in stoichiometric proportions, appears not to have been previously noticed.

The reconstruction of the Mn-terminated (111) surface may lead one to hypothesize that all Mn terminated surfaces must also contain oxygen in the termination layer for stable bonding. One may wonder, for example, whether layer mixing at the M,L-terminated (111) surface would occur, in which O migrates to the surface, to improve the coordination of the surface layer Mn ions. Such a reconstruction, however, was not observed in our room temperature molecular dynamics annealing simulations. It is possible that higher temperature annealing simulations would yield in a different reconstruction.

C. Implications for dissolution

Classical dissolution (and crystal growth) models²⁶ generally assume that dissolution (and growth) occurs primarily at steps, and is essentially negligible for flat surfaces. Our models predict low coordination numbers and oxidation

states at the surface, relative to the bulk of LiMn_2O_4 . Significant dissolution rates may require even larger coordination deficits than occur at the nominally flat surfaces addressed in this article. Such larger coordination deficits, including non-bridging oxygen, occur, for example, at steps, pits, dislocations, and edges. Consider, for example, an event at a flat surface in which a neighboring Mn^{2+} and an O^{2-} ion dissolve. We have found (Table I) that Mn has a minimum coordination number of 3 and oxygen a minimum coordination number of 2. If the two ions are bonded to each other, the total number of (M-O) bonds of the dissolving pair with the substrate that must be broken for dissolution is at least 3. In the presence of defects, such as steps, however, the required number of bonds could be lowered. Perhaps only when the number of bonds with the substrate to be broken is as low as 2 is the dissolution rate significant. Further work is necessary to explore this hypothesis.

VI. VI. CONCLUSIONS

We consider the following results of the GGA+ U simulations of lithium manganate surfaces presented in this article noteworthy:

1. The Mn-terminated (111) interface is predicted to reconstruct so as to form a top layer in which the three components are mixed in stoichiometric proportions, and the Mn is square-planar coordinated.
2. All of the terminations and orientations showed an average surface-Mn oxidation state reduced relative to the bulk.
3. Surface-Mn coordination numbers vary between 3 and 5; the oxygen coordination number (bonds to Mn) is no less than 2 at flat surfaces. Three-coordinated surface Mn is divalent.
4. The lowest energy surface is Li-terminated (001), consistent with the lowest energy surface for MgAl_2O_4 , Mg-terminated (001).

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FIG. 1: Unreconstructed surface unit cell for (111) slab. The boundaries of the computational unit cell are indicated by the dashed lines. Diamonds denote surface layer Mn atoms and squares Mn vacancies (or vice versa); O atoms in the layer below the terminating layer are represented by filled circles. Owing to the Mn surface vacancies, some O atoms are singly bonded (non-bridging), with no bonds to the termination layer. No non-bridging oxygen ions remain in the relaxed structure.

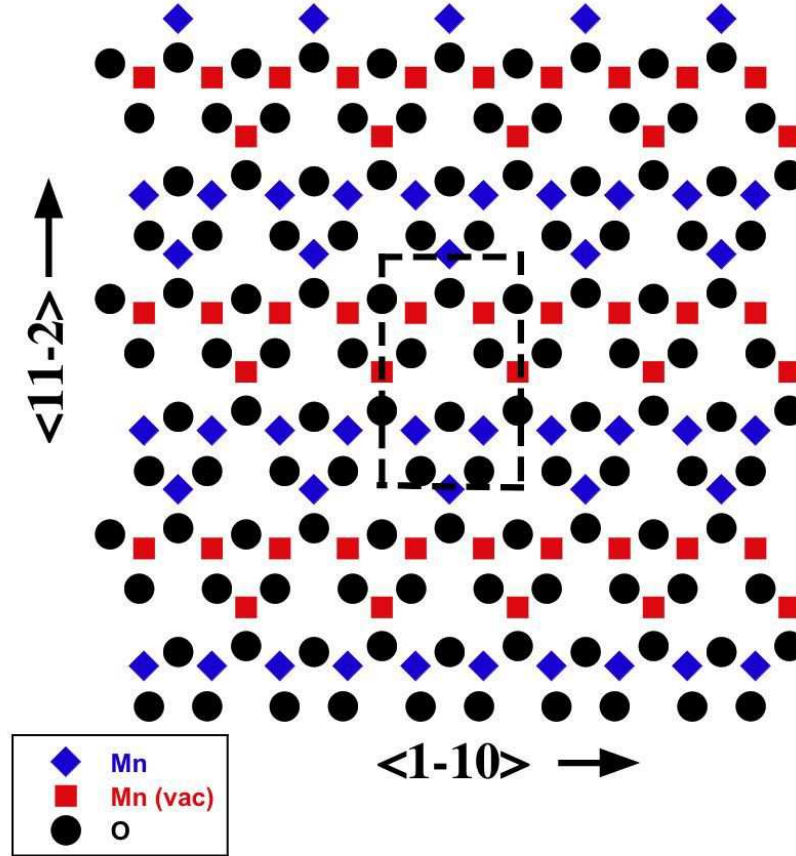


FIG. 2: Unrelaxed surface unit cell of (001) slab with MO termination. The dimensions of the periodic unit cell are indicated by the dashed lines. Large (small) diamonds (squares) denote termination layer Mn atoms (Mn vacancies); O atoms (vacancies) are represented by large (small) filled circles.

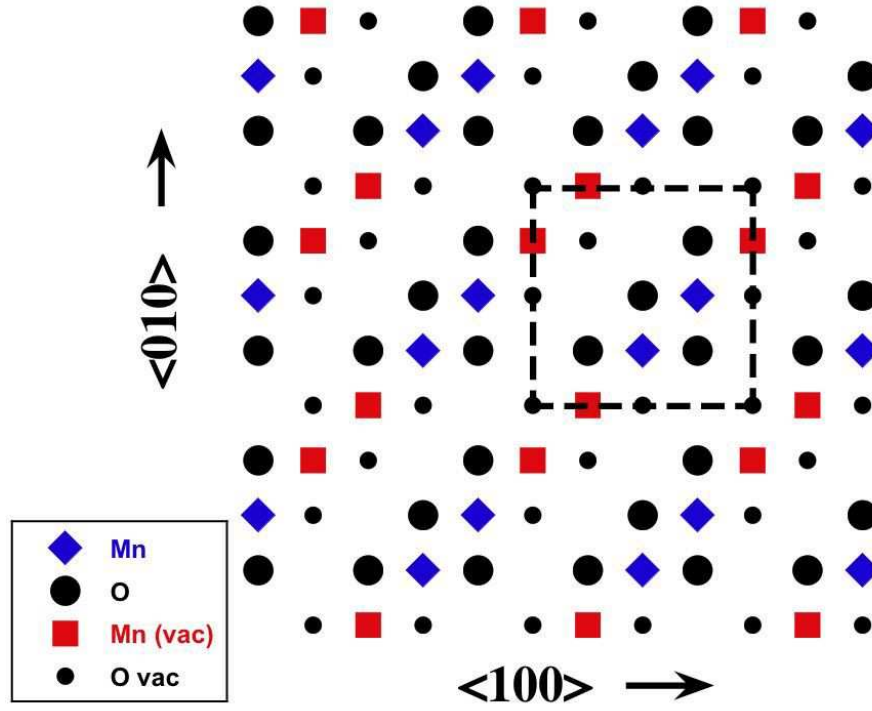


FIG. 3: Unrelaxed surface unit cell of (110) slab with MO termination. The dimensions of the periodic unit cell are indicated by the dashed lines. Large (small) diamonds denote termination layer Mn atoms (Mn vacancies); O atoms (vacancies) are represented by large (small) filled circles.

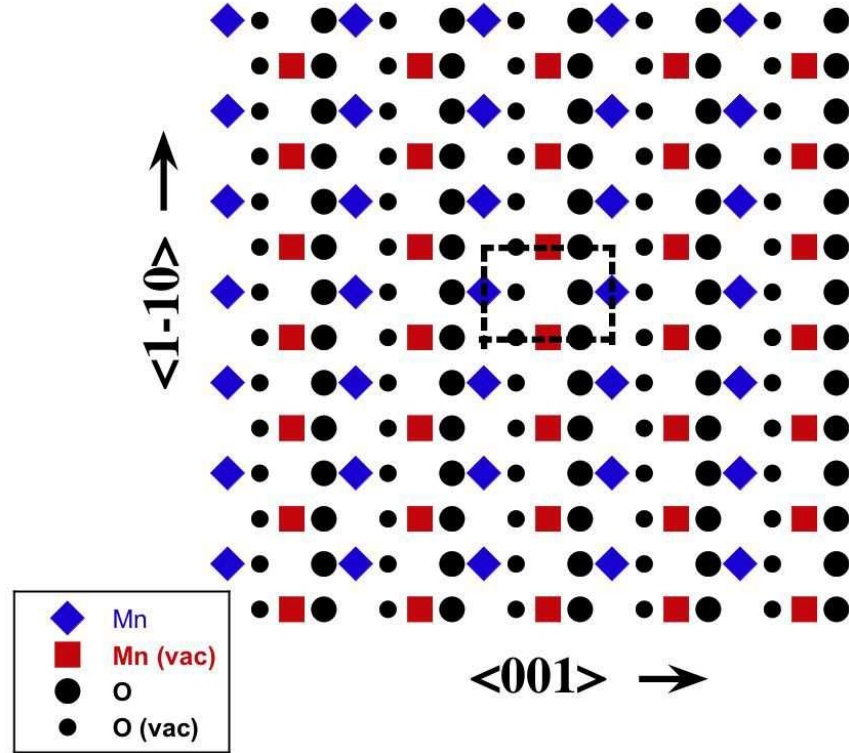


FIG. 4: Calculated cleavage energies for low index surfaces of lithium manganate.

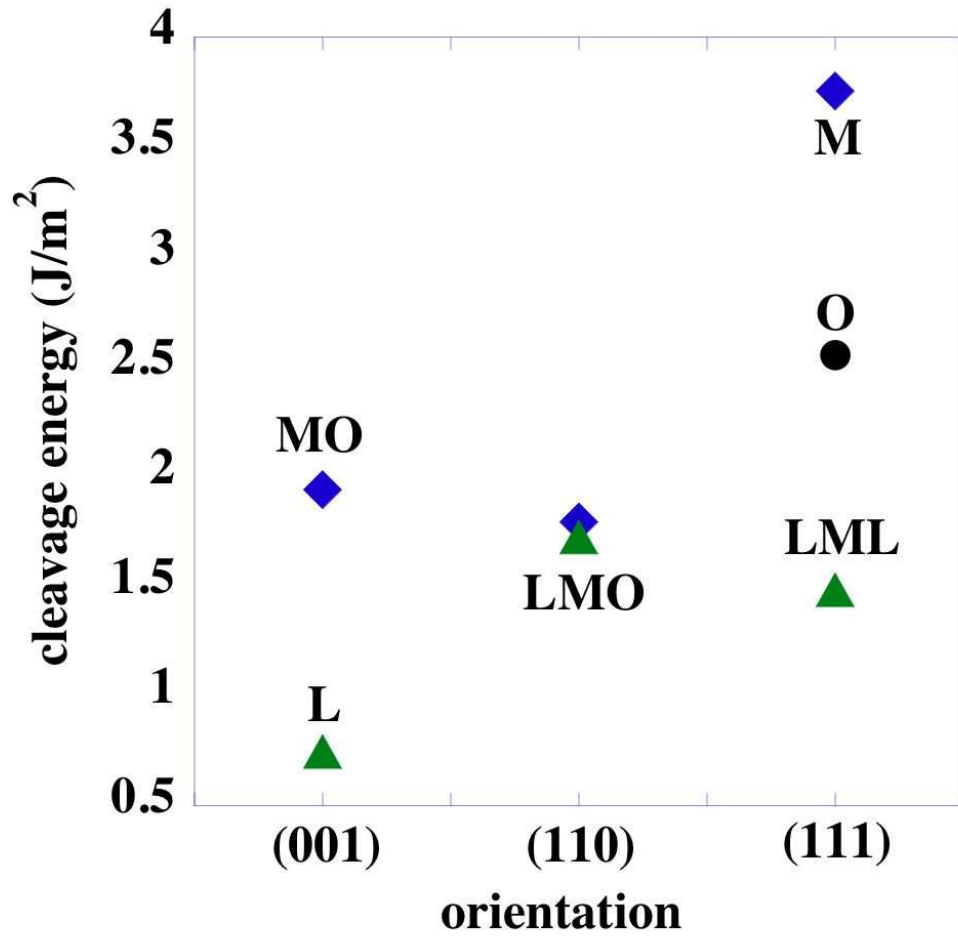


FIG. 5: Atomic arrangement of reconstructed (111) slab, projected onto a plane perpendicular to the layers. LMO termination layers contain a stoichiometric mixture of the components, in contrast to the pure layers of the unreconstructed surface (Fig. 6). The unit-cell box, with in layer axes $1\bar{1}0$ and $11\bar{2}$, is rotated by 32 degrees about the 111 axis to obtain the projection.

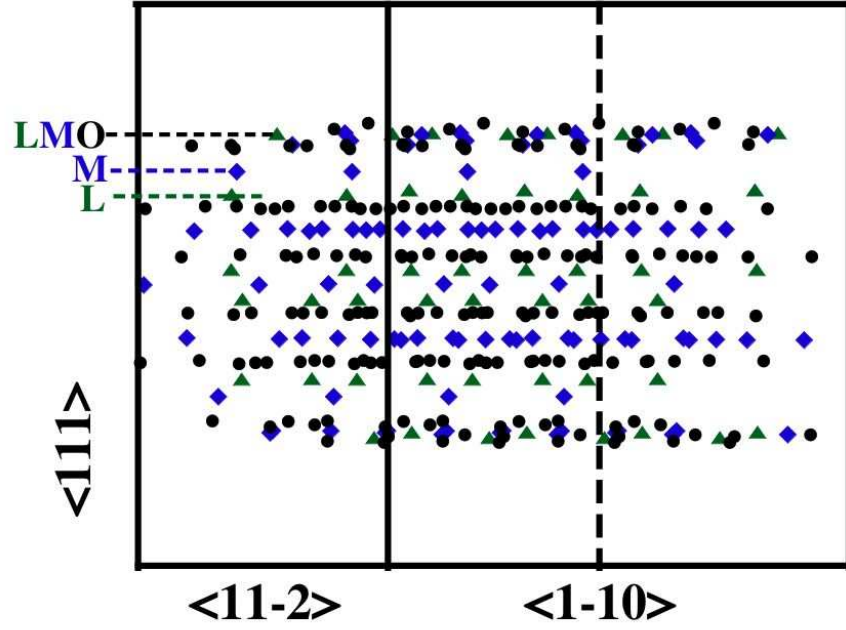


FIG. 6: Atomic positions projected onto a plane perpendicular to the layers of a (111) slab, based on simulated bulk atomic structure. The slab exemplifies layer sequence (1) in the text.

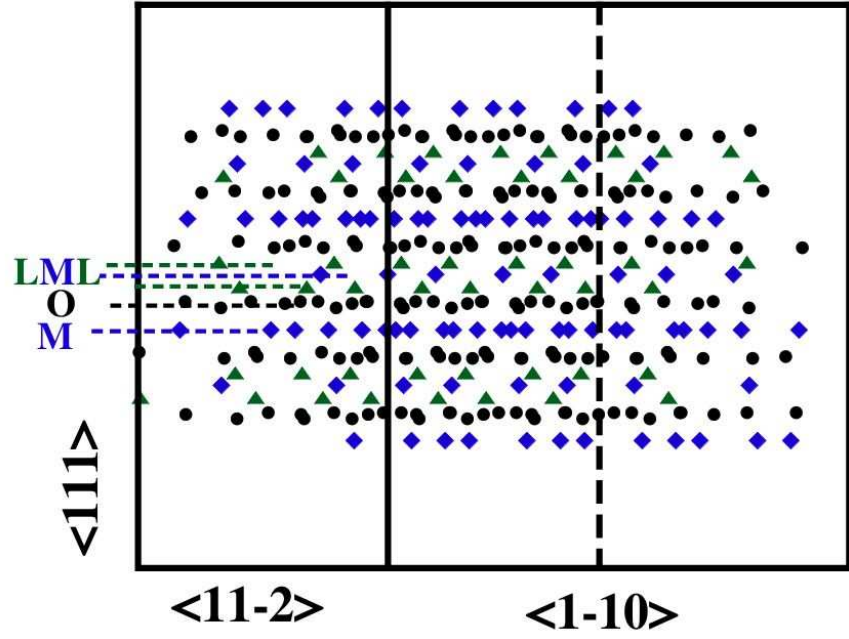


FIG. 7: Projection of atomic positions of LMO termination layer of reconstructed (111) surface. Mn ions show square planar coordination and Li ions triangular coordination.

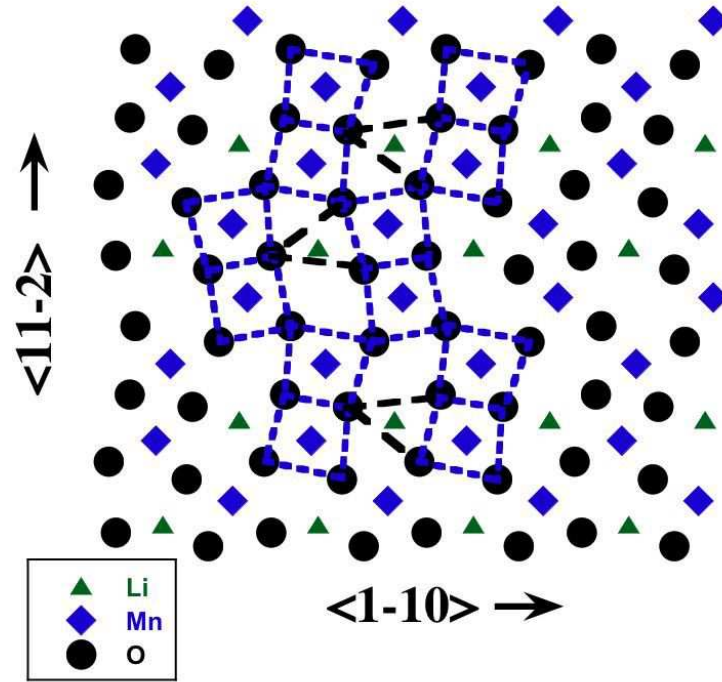


TABLE I: Coordination numbers for under-coordinated ions near a LiMn_2O_4 surface. Bulk coordination numbers are shown in the second column. Oxygen is bonded both to Mn and Li, as indicated in the bottom row.

orientation	(bulk)	(001)	(001)	(110)	(110)	(111)	(111)	(111)
termination		MO	L	MO	LMO	LMO	O	M,L
Mn	6	4;5	5	3	4,5	4	4;5	3
Li	4	3	2	3	2;3	3	3	3
O	3M,1L	2M;2M,1L	3M;2M,1L	3M;2M,1L;2M	2M;2M,1L	2M,1L;2M,2L	2M;2M,1L;3M	2M,1L;3M

TABLE II: Oxidation state of Mn ions near low index LiMn_2O_4 surfaces, for coordination numbers lower than the bulk value of 6.

CN	(001)	(001)	(110)	(110)	(111)	(111)	(111)
termination	MO	L	MO	LMO	LMO	O	M,L
3			2+				2+
4	3+			3+	3+	3+	
5		3+				3+, 4+	

TABLE III: Calculated cleavage energies, E_c , and surface energies, γ , in J/m^2 , for low index lithium manganate surfaces.

orientation	(001)	(001)	(110)	(110)	(111)	(111)	(111)
termination	MO	L	MO	LMO	LMO	O	M,L
E_c	1.94	0.75	1.79	1.72	3.76	2.55	1.48
γ	0.98	0.58	1.19	0.99	1.29	1.30	0.85
γ/E_c	0.51	0.77	0.66	0.58	0.34	0.51	0.57