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**The Combined Role of Bi-Axial Strain and Non-Stoichiometry for the Electronic, Magnetic and Redox Properties of Lithiated Metal-Oxides Films: the  $\text{LiMn}_2\text{O}_4$  Case**

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**Abstract.** Understanding the interplay between strain and non-stoichiometry for the electronic, magnetic, and redox properties of  $\text{LiMn}_2\text{O}_4$  films is essential for their development as Li-ion battery (LIB) cathodes, photo-electrodes, and systems for sustainable spintronics applications as well as for emerging applications that combine these technologies. Here, Density Functional Theory (DFT) simulations suggest that compressive strain increases the reduction drive of (111)  $\text{LiMn}_2\text{O}_4$  films by inducing  $>1$  eV upshift of the Valence Band edge. The DFT results indicate that, regardless of the crystallographic orientation for the  $\text{LiMn}_2\text{O}_4$  film, bi-axial expansion increases the magnetic moments of the Mn-atoms. Conversely, bi-axial compression reduces them. For ferromagnetic films, these changes can be substantial and as large as over 4 Bohr magnetons per unit cell over the simulated range of strain (from -6% to +3%). The DFT simulations also uncover a compensation mechanism whereby strain induces opposite changes in the magnetic moment of the Mn and O atoms, leading to an overall constant magnetic moment for the ferromagnetic films. The calculated strain-induced changes in the atomic magnetic moments reflect modifications in the local electronic hybridization of both the Mn and O atoms, which in turn suggests strain-tunable, local chemical and electrochemical reactivity. Several energy-favored (110) and (111) ferromagnetic surfaces turn out to be half-metallic with minority spin band-gaps as large as 3.2 eV and compatible with spin-dependent electron-transport, and possible spin-dependent electrochemical and electrocatalytic properties. The resilience of the ferromagnetic, half-metallic states to surface non-stoichiometry and compositional changes invites exploration of the potential of  $\text{LiMn}_2\text{O}_4$  thin-films for sustainable spintronics applications beyond state of the art, rare-earth metal based, ferromagnetic half-metallic oxides.

**Keywords:**  $\text{LiMn}_2\text{O}_4$ , biaxial strain, non-stoichiometry, batteries, redox properties, ferromagnetism, half-metallicity, spintronics.

## 1. INTRODUCTION

Lattice strain can be used to tune the electronic properties of materials and thin-films, minimizing the risk of phase transformations and detrimental effects on structural integrity and functionality.<sup>1,2</sup> The harnessing of lattice strain promises alternatives in the search for tailored materials to meet technological challenges, bypassing often expensive or hazardous synthetic approaches to modify the chemical composition of materials and manufacture nano-engineered interfaces.<sup>3</sup> Controlled use of lattice strain has been successfully implemented and shown to be beneficial in fields as diverse as semiconductor electronics,<sup>4</sup> topological insulators,<sup>5</sup> photocatalysis,<sup>6,7</sup> metal- and metal-oxide based catalysis and corrosion protection,<sup>8–11</sup> oxygen electro-catalysis and electrochemistry,<sup>1,2,12,13</sup> as well as ion-diffusion in lithium-ion batteries (**LIBs**).<sup>14,15</sup>

In spite of these advances, the interplay between lattice strain and non-stoichiometry in metal-oxide surfaces for the emerging electronic, magnetic and redox-chemistry properties remains overlooked. This has prevented the development of guidelines for combined use of strain and non-stoichiometry to tune the redox chemistry of metal-oxide surfaces *and/or* promote the emergence of bespoke electronic and magnetic surface properties. This situation is particularly unfortunate for LIBs,<sup>16</sup> where control of the reactions at the electrode/electrolyte interface is essential for the stability of the electrode-electrolyte interphases (solid electrolyte interphase, **SEI**, at the anode, and cathode electrolyte interphase, **CEI**, at the cathode)<sup>17,18,19,20,21,22,23</sup> that are critical for the performance and lifetime of devices. Such a knowledge gap also prevents rational, expedited progress in the fields of oxide-based photo-electro-catalysis,<sup>3,24,25</sup> oxide-based sustainable spintronics,<sup>26,27,28</sup> and, critical for the present study, at the interface between these areas of research and their focus on *different* chemical and physical properties of the *same* (or compositionally similar) oxides.

As hybrid technologies based on combination of diverse electrochemical, opto-electronic and magnetic functions for a given material begin to emerge,<sup>26,27,28,29</sup> their optimization and uptake

require fundamental computational studies with an integrative, holistic approach to the combination and interplay of different materials properties. We believe this emerging class of hybrid applications also invites computational studies targeted at screening the material-specific dependence on intrinsic and extrinsic factors of the *interplay* between specific chemical and physical properties of interest.

To this end, here we use Density Functional Theory (**DFT**) to explore and quantify the interplay between bi-axial lattice strain and surface non-stoichiometry for the electronic, magnetic, and redox properties of an archetypal lithiated metal-oxide: spinel  $\text{LiMn}_2\text{O}_4$ .  $\text{LiMn}_2\text{O}_4$  is an alternative cathode material for high-power electromotive applications of future LIBs.<sup>30</sup> Despite the vast research in  $\text{LiMn}_2\text{O}_4$  cathodes,<sup>31-34</sup> the reaction mechanisms at the surfaces of this material remain debated and poorly controlled, resulting in its degradation upon cycling and impeding its commercial uptake.<sup>35</sup>

In recent years, the use of ultra-high vacuum epitaxial growth has benefited experimental research in surface chemistry and spintronics by enabling controlled manufacturing of relatively flat ultra-thin films with the desired composition, crystallographic phase and orientation.<sup>17,18,26,36, 37</sup>

Epitaxial growth can also induce strain in thin-films by lattice misfit at the interface with the supporting substrate.<sup>38</sup> Experiments on  $\text{LiMn}_2\text{O}_4$  thin-films grown over  $\text{SrTiO}_3$  demonstrate that the film's (electro-)chemical properties are critically dependent on the crystallographic orientation.

Whereas electrolyte wetting of the (111) surface leads to CEI formation, wetting of the (110) facet induces dissolution of  $\text{Mn}^{+2}$  into the electrolyte, even at zero-voltage conditions i.e. in the absence of an externally applied voltage. The facet-dependent electrochemistry of  $\text{LiMn}_2\text{O}_4$  films may also be relevant for electrochemically controlled, sustainable hybrid-spintronics applications. This new class of applications has been recently demonstrated using electrochemically induced ion-diffusion in sub-stoichiometric manganese oxides ( $\text{MnO}_x$ ) films interfaced with molecular films under potentiostatic control.<sup>27</sup> These considerations provide further motivations for our interest in the

dependence of the magnetic properties of  $\text{LiMn}_2\text{O}_4$  films on both strain and non-stoichiometry.

Finally, continuous progress in the synthesis and modification of piezoelectric thin-films<sup>39-42</sup> holds great promise for their use also as deposition substrate for functional films and *dynamic* external control of strain therein. Development and optimization of such approaches to dynamic property-tuning in functional films, possibly also in conjunction with electrochemical intercalation, self-evidently require understanding of the interplay between electrochemical and magnetic properties for a given material, which we start contributing here for  $\text{LiMn}_2\text{O}_4$  films. We thus expect the present findings on the interplay between non-stoichiometry and strain for the electronic, magnetic and redox properties of  $\text{LiMn}_2\text{O}_4$  films to be valuable for a wide readership with applicative interests in LIB-cathodes, (photo-)electro-catalysis and sustainable spintronics applications as well as in emerging hybrid technologies at the intersection between these currently minimally connected areas.

## 2. COMPUTATIONAL METHODS

Fully unconstrained, spin-polarized Density Functional Theory (DFT) calculations were carried out using the anisotropic (U-J) approach<sup>43</sup> with periodic boundary conditions (PBCs) and the projector-augmented wave method as implemented in the VASP program.<sup>44,45</sup> Based on our previous work on vacuum-exposed LMO surfaces,<sup>31</sup> we used the GGA-PW91 approximation<sup>46</sup> for the electronic exchange-correlation (XC) interaction, including the interpolation formula of Vosko et. al.,<sup>47</sup> with  $U=6.2$  eV and  $J=1.2$  eV anisotropic Hubbard corrections for the  $3d$  orbitals of the Mn atoms.<sup>31,48</sup> As benchmarked in Ref. 48, anisotropically (U-J) corrected GGA-like XC-functionals (as used here) can describe the magnetic properties and underpinning electronic hybridization in Mn-oxides with an accuracy comparable to that of hybrid DFT, resulting in semi-quantitative agreement between calculated and experimental results. The suitability of the adopted DFT+(U-J) approach in modeling strain-dependent semiconductor-to-metal transitions for  $\text{LiMn}_2\text{O}_4$  slabs was validated against

screened hybrid-HSE06<sup>49</sup> results for the stoichiometric (110) slab. Owing to the increased computational cost of the HSE06 simulations in comparison to the DFT+(U-J) ones, these benchmarks were carried out on slabs of reduced thickness (56 atoms, 8 LiMn<sub>2</sub>O<sub>4</sub> units arranged in 8 atomic layers). Based on recent benchmarking of the (overestimated) description of the band-gap for bulk LiMn<sub>2</sub>O<sub>4</sub> by the standard HSE06 XC-functional with 25% Hartree-Fock (HF) mixing,<sup>50</sup> and following standard procedures for fine-tuning of the HF-mixing on experimental band-gaps,<sup>51</sup> this validation was carried out with 10.5% (not 25%<sup>49</sup>) HF-mixing. Such HF-mixing was tested to recover the experimental band-gap for bulk LMO (1.2 eV<sup>50</sup>). The interested reader is referred to the Supporting Information (Section SI-6, Table S2) for further details.

Dispersion interactions were included via the van der Waals (vdW)-corrected DFT formalism with the parametrization proposed by Grimme,<sup>52</sup> and a global scale factor equal to 0.7 for the PW91 exchange-correlation functional.

We assumed the LiMn<sub>2</sub>O<sub>4</sub> crystal in its cubic phase, which is the phase observed for operational temperatures of LIBs. A vacuum buffer of at least 12 Å was included to avoid spurious interactions between opposite surfaces of the PBC-replicated slabs.

Electronic energies were converged within tolerances of 10<sup>-4</sup> eV for a plane-wave energy cutoff of 550 eV. The 2D Brillouin zones were sampled using the Monkhorst-Pack scheme with 3x3 k-points for the (001) and (110) surfaces, whereas 2x4 k-points were used for the (111) surface. All atomic positions were relaxed until the ionic forces became lower than 0.03 eV/Å. Following previous research in reducible transition metal-oxides,<sup>53,54</sup> Mn<sup>+4</sup>, Mn<sup>+3</sup> and Mn<sup>+2</sup> sites were identified from the computed atomic magnetic moments.<sup>31,69</sup>

All the simulated stoichiometric slabs were composed of 168 atoms (24 LiMn<sub>2</sub>O<sub>4</sub> units), arranged in 24 atomic layers and with optimized thicknesses in the 2.66-2.84 nm range. These were checked to be sufficiently large to yield surface energies converged to within 0.01 J/m<sup>2</sup>.<sup>31</sup> To cancel the

inherent perpendicular dipole moment of these polar slabs, we applied the Tasker method<sup>55</sup> by transferring atoms between opposite surfaces of the slabs.<sup>31</sup> All the slab models are symmetric along the z-axis, perpendicular to the surface (see Section SI-5). This symmetry condition ensures dipole-free slabs and excludes the need to apply dipole corrections. The procedures followed to build the non-stoichiometric slabs and to calculate their relative thermodynamic stability are detailed in the Supporting Information (Sections SI-8 and SI-9). We note that the present study is not focused in comparing the relative stability between different facets of the  $\text{LiMn}_2\text{O}_4$  films. Instead, we are interested in epitaxially grown  $\text{LiMn}_2\text{O}_4$  films, where the surface orientation of the film is determined by the crystallographic structure of the deposition substrate.<sup>18</sup> Depending on the lattice misfit between the  $\text{LiMn}_2\text{O}_4$  films and the deposition substrate, the films will be exposed to tensile or compressive strains as studied here. Finally, we note that the stoichiometric models of the (001), (110) and (111) slabs in Figs. 1-2 have the same number of atoms, which enables direct comparison of their relative energy, should the reader be interested in so doing. The same does not hold for the non-stoichiometric models in Figs. 3-4.

Following checks on the quantitatively negligible dependence of the strain-induced changes in atomic magnetic moments on the (projection or volume-integration) protocol used to integrate the spin-density (Section SI-7, Fig. S11), and unless otherwise stated, all the atomic magnetic moment were calculated by projection of the spin-density into the PAW-core using the default VASP PAW-projectors.

In the following, we define the bi-axial strain (epitaxial lattice misfit) as:

$$\varepsilon^{(i)}(s^{(i)}) = (s^{(i)} - s_0^{(i)})/s_0^{(i)} ,$$

where  $s^{(i)}$  and  $s_0^{(i)}$  correspond to the absolute value (module) of the two surface lattice vectors ( $i=1,2$ ) of the strained and strain-free film, respectively. In this work, we assume that  $\text{LiMn}_2\text{O}_4$  films form a coherent interface with its supporting substrate. Thus, the surface vectors of the strained film



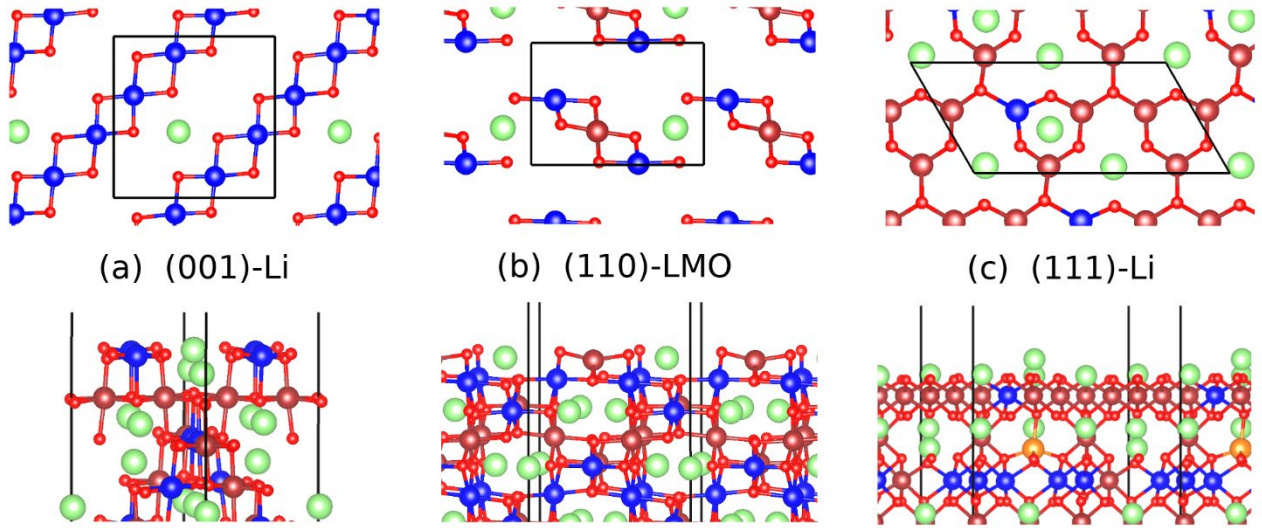
( $\vec{s}^{(1)}$  and  $\vec{s}^{(2)}$ ) are the same as (or commensurate with) the surface vectors of the supporting substrate. This approximation is justified by the results of X-Ray Diffraction (XRD) experiments on air-exposed  $\text{LiMn}_2\text{O}_4$  films supported by  $\text{SrTiO}_3$ ,<sup>18</sup> and excludes any possible change in the angle formed by the surface vectors for this type of systems. Although we do not include the supporting substrate explicitly in our simulations, we assume any bi-axial strain exerted over the film is such that it preserves the symmetry of the supporting substrate. The formulation in Section SI-13 demonstrates that this assumption is only valid when misfits  $\epsilon^{(1)}$  and  $\epsilon^{(2)}$  are the same, and this achieved when the surface vectors are scaled by the same factor, while keeping their orientations fixed.

### 3. RESULTS AND DISCUSSION

#### 3.1 Stoichiometric (001), (110) and (111) $\text{LiMn}_2\text{O}_4$ surfaces

Here we focus on the (001), (110) and (111) facets of  $\text{LiMn}_2\text{O}_4$  that are energetically favored in vacuo. We first consider stoichiometric surfaces in the canonical ensemble approximation.

In agreement with previous results for  $\epsilon=0$ ,<sup>31</sup> we find that the lowest energy (001), (110) and (111) facets are Li [(001)-Li], Li-Mn-O [(110)-LMO] and Li terminated [(111)-Li], respectively (Figure 1). Once relaxed, (001)-Li and (110)-LMO contain the same amount of (high-spin)  $\text{Mn}^{+3}$  and (low-spin)  $\text{Mn}^{+4}$  sites in the slab. In contrast, (111)-Li hosts additional (very high-spin) sub-surface  $\text{Mn}^{+2}$  sites, introduced by the inverse spinel reconstruction (SI-4) and ensuing disproportionation.<sup>31</sup>



**Figure 1.** Top and side views of the optimized atomic structure for the lowest-energy, stoichiometric surfaces of  $\text{LiMn}_2\text{O}_4$ : **(a)** (001)-Li, **(b)** (110)-LMO, **(c)** (111)-Li. For clarity, only the two outermost layers are displayed in the top views. The black lines mark the periodicity of the simulation cells.  $\text{Mn}^{+3}$ : blue,  $\text{Mn}^{+4}$ : maroon,  $\text{Mn}^{+2}$ : orange, O: red, Li: green.

Figure 2a shows the computed relative energies for the ferro-magnetic (**FM**) and anti-ferro-magnetic (**AFM**) ground-state solutions of the systems studied as a function of  $\epsilon$ . For  $\epsilon \geq 0$ , and regardless of the magnetic ordering, (111)-Li is consistently favored ( $\geq 2$  eV) over the other terminations. However, compression ( $\epsilon < 0$ ) progressively reduces the (111)-Li favorability until  $\epsilon \lesssim -2\%$ , for which (001)-Li becomes the lowest energy surface. From being favored at zero-strain, (111)-Li turns into the highest-energy surface for  $\epsilon \lesssim -4\%$ . Regardless of the surface termination, FM ordering is systematically favored for tensile ( $\epsilon > 0$ ) strain. Conversely, AFM ordering is favored by compression ( $\epsilon \lesssim -2/-3\%$  depending on the surface, see also Figure S5). Strain can accordingly alter the relative energy of  $\text{LiMn}_2\text{O}_4$  surfaces in both FM and AFM ordering, offering potential avenues to controlled engineering of magnetic ordering for  $\text{LiMn}_2\text{O}_4$  thin films grown on suitably mismatched deposition substrates.

With the only exception of the AFM solution for (001)-Li, the atomic magnetic moments for the Mn and O atoms are strongly sensitive to strain (Figures 2c-d and S6-S8). Compression (expansion) is found to systematically decrease (increase) the magnetic moment of the Mn-atoms in the film, regardless of their oxidation state and overall magnetic ordering. As the rate of change with the applied strain is roughly the same for the AFM and FM solutions, the FM systems preserve their larger atomic magnetic moments by comparison to the AFM counterparts (Figures S6-S7). Notably, the simulations reveal a compensation mechanism whereby the changes in the magnetic moment of the O-atoms cancel those at the Mn-sites, leading to an overall constant slab-magnetic moment for the FM solutions across the whole range of  $\epsilon$  studied. Based on this mechanism, strain could be used to separately tune the local electronic hybridization (oxidation state<sup>53,54,56</sup>) and magnetism of the O- and Mn-sites at  $\text{LiMn}_2\text{O}_4$  surfaces, potentially altering the local chemical reactivity towards those spin-polarized species that are inevitably present in multi-electron electro-photo-catalytic processes.<sup>1,2, 6–13,57,58</sup> As detailed in Section SI-7 (Fig. S11), we tested numerically that the calculated changes in atomic magnetic moments with strain do not depend on the method (PAW-projectors, radially truncated spherical harmonics, and Bader decomposition) used for atom-specific integration of the spin-density. The calculated changes should therefore be physical and not due to numerical artefacts.

Remarkably, whereas the FM and AFM solutions for (001)-Li and (111)-Li remain semiconducting for the whole range of  $\epsilon$  studied, (110)-LMO in FM ordering becomes half-metallic for  $\epsilon \lesssim -2\%$  (Figure S10). In the simulations, the minority-spin band-gap for this surface decreases linearly from 2.09 eV to 2.4 eV as the compressive strain is increased (in absolute value) from  $\epsilon = -2\%$  to  $\epsilon = -6\%$ . These band-gap values are over 1.3 eV larger than the results for bulk cubic  $\text{LiMn}_2\text{O}_4$  at the same level of theory (FM: 0.71 eV, AFM: 1.09 eV),<sup>31</sup> suggesting that strain in thin films can be used to open band-gaps beyond the bulk limit.

Given the absence of any Self-Interaction Error correction on the O-atoms, the DFT+(U-J)

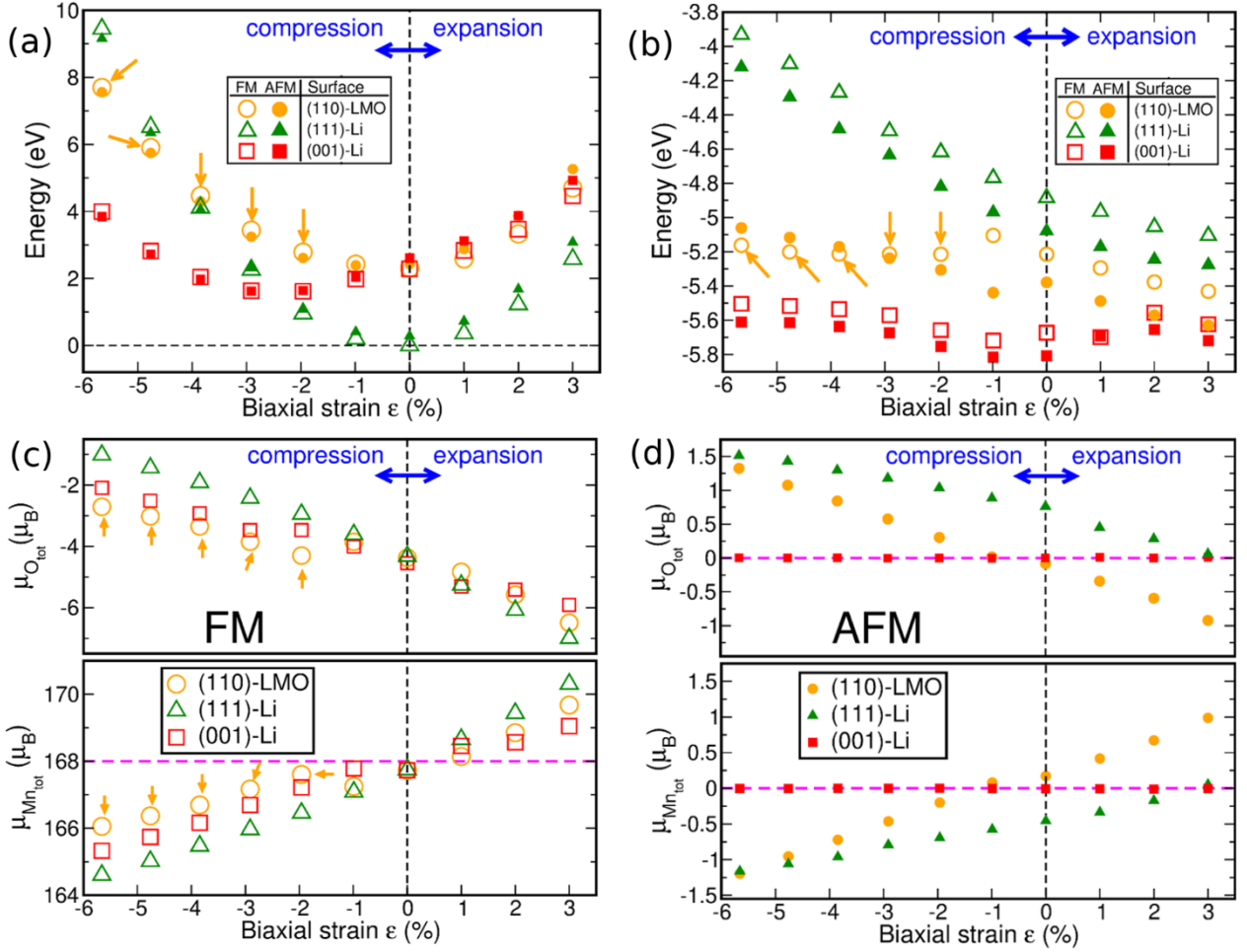
semiconductor-to-metal transition visible in Fig. S10 for the stoichiometric (110) slab in FM ordering for  $\epsilon \leq -2\%$  requires additional validation, which we provide in the following using screened hybrid HSE06<sup>49</sup> results as reference.

Table S2 compares the calculated Kohn-Sham (direct) band-gaps for the stoichiometric (110) slabs at selected values of lattice misfit  $\epsilon$  (-6%, 0%, +3%) and for different simulations set-ups. As indicated by the appearance of zero band-gaps (non-zero Density of States at the Fermi energy), simulation at DFT+(U-J) and HSE06 (10.5% and 12.5% HF mixing) level of both the DFT+(U-J) and HSE06 optimized geometries for compressive lattice misfits ( $\epsilon=-6\%$ ) results in the appearance of (half-)metallic solutions. Whereas 10.5% HF mixing leads to a fully metallic solution, slight increase of HF-mixing to 12.5% results in a half-metallic system, as modeled at DFT+(U-J) level. The quantitative dependence of the calculated band-gaps on the HF-mixing is clearly both inevitable and unsurprising. However, the persistence of the compression-induced semiconductor to (half-)metal transition in both the DFT+(U-J) and screened hybrid DFT results provides confidence the computed effect should be qualitatively correct and, consequently, of potential significance in further developing LiMn<sub>2</sub>O<sub>4</sub> films for applications that depend on electron- and/or spin-transport.

With band-gaps for minority spin electrons in excess of 2.4 eV, the calculated half-metallicity of compressed (110)-LMO with FM ordering should result in strongly spin-dependent electron-transport properties. This is justified considering that the computed minority spin band-gaps for compressed LiMn<sub>2</sub>O<sub>4</sub>(110) films ( $\geq 2.4$  eV) are actually larger than for a state of the art half-metallic ferromagnets such as La<sub>0.7</sub>Sr<sub>0.3</sub>MnO<sub>3</sub> (2 eV<sup>59</sup>), a system heavily studied due to its spin-dependent electron transport properties. These results invite further research in compressed LiMn<sub>2</sub>O<sub>4</sub> films for potential applications in spin-filtering devices<sup>26-28</sup> or as an alternative to re-hybridization with organic molecules to generate half-metallicity in Mn-oxide films.<sup>27</sup>

While the results of the simulations require experimental verification, the emergence of spin-

dependent electronic transport properties in compressed  $\text{LiMn}_2\text{O}_4$  films also posits that the systems' electrochemistry will be affected. This because, pending “contact potential” considerations,<sup>20,21,22,60</sup> application of external voltages smaller than the minority band-gap will inevitably populate only the majority spin bands resulting in surface excess charge of, at least initially, only one spin in contrast to the standard *diamagnetic* charging (same concentration of excess carriers for both electron spins).



**Figure 2.** (a) Relative energies, (b) vacuum-aligned VBEs, and atom-resolved total magnetic moments (c-d) for the lowest energy stoichiometric  $\text{LiMn}_2\text{O}_4$  surfaces as a function of bi-axial strain ( $\epsilon$ ) and (FM or AFM) magnetic ordering. The orange arrows point to the half-metallic solutions for compressed (110)-LMO. The pink horizontal lines in panels (c) and (d) mark the total magnetic moment of the slabs.

To investigate qualitatively the reduction drive of these systems, we align their Valence Band edge (VBE) to the vacuum level (Figure 2b). Although the vacuum-aligned VBEs in Fig. 2b neglect critical thermodynamics and kinetics effects due to dynamic relaxation at the solid-electrolyte interface and ensuing contact potential,<sup>20,21,22,60</sup> they do allow direct comparison of the intrinsic energy drive to donate electrons for different systems.<sup>31,61,62</sup> For the sake of clarity, we reiterate that, in the absence of values for the corresponding contact potential,<sup>20,60</sup> the vacuum aligned VBEs (or workfunction for the metallic systems) cannot be immediately related to the absolute electrochemical potential of the  $\text{LiMn}_2\text{O}_4$  films.

Moreover, although indicative of the energy drive to electron transfer (in vacuo),<sup>62</sup> the calculated vacuum-aligned VBEs do not provide any quantitative information on the electrochemical mechanisms (kinetics included) of formation for passivation layers (CEI) on  $\text{LiMn}_2\text{O}_4$  cathodes. In spite of all these limitations, the vacuum-aligned VBEs in Fig. 2b allow direct comparison of the combined role of surface-termination and strain in altering the energy position of the (adiabatic) electron-donor states of the systems. To the best of our knowledge, this aspect has not been previously considered in the literature on  $\text{LiMn}_2\text{O}_4$  cathodes, although potentially relevant for future molecular-dynamics based studies of the thermodynamics and kinetics factors that need to be considered for quantitative understanding of the formation of passivation layers on battery electrodes.<sup>20</sup>

For  $\epsilon=0$ , and regardless of the magnetic ordering, the VBE for (111)-Li is  $\sim 0.3$  eV and  $\sim 0.8$  eV higher than for (110)-LMO and (001)-Li, respectively, indicative of a larger reductive energy drive. The response of the VBE to compression turns out to be strongly facet-dependent. The VBEs remain practically unaltered for (001)-Li and (110)-LMO. Thus, the simulation indicates that application of strain should not be effective in tuning the reduction energy drive of the stoichiometric (001)-Li and (110)-LMO surfaces. In contrast, compression upshifts the VBE of (111)-Li by up to 0.4 eV ( $\epsilon \sim 3\%$ ) and  $\approx 1.0$  eV ( $\epsilon \sim 5.7\%$ ) with respect to the  $\epsilon=0$  result. Thus,

compressive strain is calculated to enhance significantly the reduction drive of the stoichiometric (111)-Li surface. In general, the VBEs for the FM solutions are always slightly higher ( $\leq 0.2$  eV) than for the AFM ones, indicating a slightly larger reduction drive for FM ordering. Conversely, we find the Conduction Band edge (**CBE**) for the FM solutions to be lower than for the AFM ones (Figure S9), leading to narrower FM band-gaps, independently of the strain (Figure S10). These trends are in line with earlier results for bulk  $\text{LiMn}_2\text{O}_4$  at the same level of theory.<sup>31,48</sup>

In both our previous<sup>31</sup> and present simulations, we find that the VBEs for all the  $\text{LiMn}_2\text{O}_4$  slabs are dominated by O(2p) states with smaller yet non-negligible contributions from Mn(3d) states. It thus follows that all the different  $\text{LiMn}_2\text{O}_4$  slabs in Fig. 1 have their O(2p)-VBE in close proximity to the Fermi level. Based on a recent model for ethylene carbonate (EC) dissociation on the surfaces of both layered and rocksalts oxide surfaces (developed with no direct simulation of  $\text{LiMn}_2\text{O}_4$  surfaces),<sup>19</sup> all the terminations for  $\text{LiMn}_2\text{O}_4$  films in Fig. 2b should exhibit a comparably strong energy drive to EC dissociation. However, such a hypothesis is in contrast with what was measured for differently oriented  $\text{LiMn}_2\text{O}_4$  films exposed to a 1 M  $\text{LiPF}_6$  electrolyte in an EC/diethyl carbonate (DEC) solution with molar ratio of 3:7.<sup>18</sup> As a result of this discrepancy, and since different  $\text{LiMn}_2\text{O}_4$  surfaces were not included in the development the O(2p)-band model in Ref. 19, we believe absolute alignment to a common reference (the vacuum level) for the VBE of the  $\text{LiMn}_2\text{O}_4$  films presents advantages over the dissociation energy of EC for comparing the electron-donor levels of different surfaces as a function of strain.

However, it should be noted also that the vacuum-aligned VBEs in Fig. 2b do not allow any conclusion on the role of strain for the competition of different adsorption mechanisms of EC on  $\text{LiMn}_2\text{O}_4$  films nor for the atomistic mechanism of formation for passivation layers on  $\text{LiMn}_2\text{O}_4$ . To this end, and based on the markedly different response to strain for the O(2p)-dominated VBE of different  $\text{LiMn}_2\text{O}_4$  surfaces in Fig. 2b, it remains to be assessed the extent to which and how strain may alter the competition between different adsorption pathways on this material and the

applicability of the O(2p)-model for strained  $\text{LiMn}_2\text{O}_4$  cathodes. We hope our results and the present considerations will stimulate future work in the subject, which is clearly beyond the primary scope of this paper: the role of strain in tuning the interplay between electronic and magnetic properties for  $\text{LiMn}_2\text{O}_4$  films.

As shown in Fig. 2b, the VBE for (111)-Li at  $\varepsilon \approx 6\%$  is roughly 1 eV higher than for the unstrained systems at  $\varepsilon = 0\%$ , indicative of a substantially larger energy drive for electron transfer towards interacting molecules. This may play a role in the experimentally observed *zero-voltage* decomposition of the electrolyte on (111) surfaces.<sup>17,18</sup> However, X-Ray Diffraction (XRD) experiments on air-exposed  $\text{LiMn}_2\text{O}_4(111)$  films previous to electrolyte wetting reveal bulk-like lattice parameters for the films ( $7.32 \pm 0.58$  nm thick),<sup>17</sup> which ultimately prevents direct comparison with our calculations on vacuum-exposed (2.66-2.84 nm thick) *strained* models. Clearly, DFT simulations of  $>7$  nm thick slabs are impractically demanding, if not prohibitive. Therefore, further photoemission or electrochemical experiments on thinner  $\text{LiMn}_2\text{O}_4$  film with XRD-confirmed strain would be needed to quantitatively validate the present results and their significance for the actual mechanisms of *zero-voltage* electrolyte decomposition on  $\text{LiMn}_2\text{O}_4(111)$ .

### 3.2 Non-stoichiometric (001), (110) and (111) $\text{LiMn}_2\text{O}_4$ surfaces

During the synthesis of  $\text{LiMn}_2\text{O}_4$  films, the experimental conditions are inevitably adjusted to follow a given protocol, which causes deviations from the canonical ensemble, that is constant-particle, volume and temperature approximation we have assumed until now.<sup>33</sup> Thus, we next turn to simulations in the grand canonical ensemble to model a more realistic scenario where the system exchanges particles (atoms) with the environment, potentially resulting in non-stoichiometric surfaces, at constant chemical potential, volume and temperature. To this end, we quantify the relative stability of different  $\text{LiMn}_2\text{O}_4$  surfaces as a function of strain *and* departure of the chemical

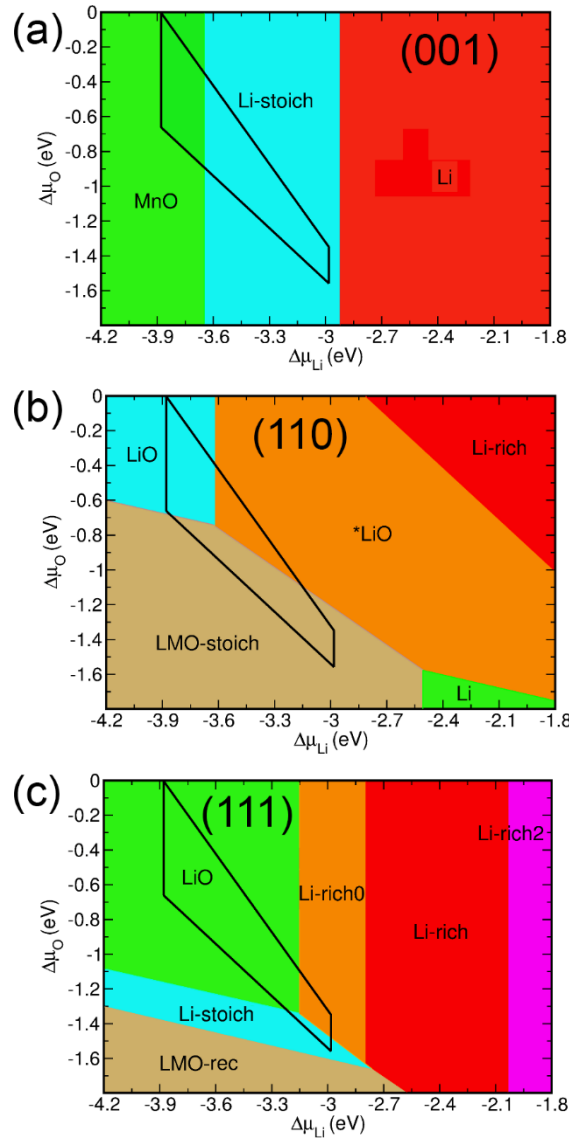


potentials of the constituent atoms ( $\Delta\mu_\alpha$ ) from their standard reference values  $\mu_\alpha^S$  ( $\alpha=\text{Li, Mn, O}$ ). Details of the simulated surfaces are provided in Section SI-9. Due to the relatively small energy differences between the FM and AFM ordering of the stoichiometric surfaces (Figures 2 and S5), and to contain the computational cost, we limit this study to the FM solutions. For the analysis, we set  $\Delta\mu_{\text{Li}}$  and  $\Delta\mu_{\text{O}}$  as the two independent thermodynamic variables, with  $\Delta\mu_{\text{Mn}}$  being defined by the stability condition of bulk  $\text{LiMn}_2\text{O}_4$  (Sections SI-2 and SI-8).

Figure 3 reports the stability phase diagrams for different terminations of the (001), (110) and (111) facets at zero-strain ( $\epsilon=0$ ) as a function of the changes in the chemical potential of the Li ( $\Delta\mu_{\text{Li}}$ ) and O ( $\Delta\mu_{\text{O}}$ ) atoms. As discussed in Section SI-2, the region of thermodynamic stability for bulk  $\text{LiMn}_2\text{O}_4$  with respect to competing Mn-oxides is contained within the black polygons. The stoichiometric surfaces (*stoich*) analyzed in Figures 1 and 2 turn out to be energetically favored over a relatively limited region of the chemical-potential space. The computed phase diagrams for the (001) and (111) facets agree qualitatively with the findings of Ref. 33 at zero-strain. However, some deviations for the (110) facet appear. This reveals a non-negligible dependence of the results on the XC-functional (PW91 here, PBE in Ref. 33) and anisotropic (present case) or isotropic (in Ref. 33) Hubbard corrections, as typical for correlated Mn-oxides.<sup>31,48,63</sup> For the interested reader, the Supporting Information (SI-10) provides an extensive analysis of these differences.

Notably, we find that the region of stability for each termination to be strongly sensitive to the applied strain  $\epsilon$ , with the stoichiometric terminations of the (001) and (111) facets becoming unstable for substantial compression ( $\epsilon < -4.76\%$ ), as indicated by their disappearance from the phase-stability diagrams (Figs. S16-S17). These results suggest that, depending on the strain introduced in  $\text{LiMn}_2\text{O}_4$  thin-films, *different* non-stoichiometric surfaces could be engineered for the *same* protocol of film preparation. In principle, different strain in  $\text{LiMn}_2\text{O}_4$  films may be introduced both *statically* by changing the epitaxial growth substrate and *dynamically* in the presence of piezoelectric properties for the growth substrate itself<sup>39-42</sup> or reversible electrochemical lithiation.<sup>30-</sup>

<sup>35</sup> As these approaches are experimentally viable for metal-oxide thin-films,<sup>30-35,39-42</sup> experimental validation of our results may be within reach and of potential significance for the diversified communities interested in functional films for LIB-electrodes, photo-electro-catalysis and sustainable spintronics applications.



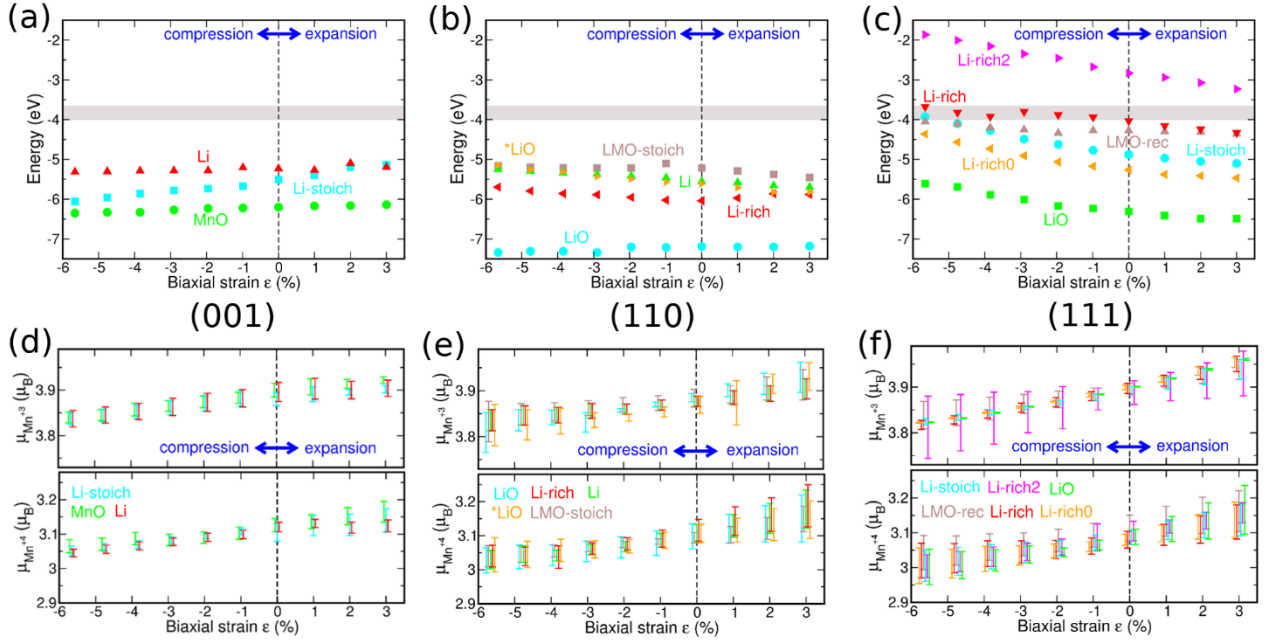
**Figure 3.** ( $\Delta\mu_{Li}$ ,  $\Delta\mu_O$ ) dependent stability phase diagrams for the different terminations of the (a) (001), (b) (110) and (c) (111) surfaces at zero-strain ( $\epsilon=0\%$ ). The black polygon indicates the region of thermodynamic stability for bulk  $\text{LiMn}_2\text{O}_4$  with respect to competing Mn-oxides (Figure S2). The fully relaxed atomic structures for each surface termination are shown in Figs S19 to S21.

Figure 4a-c report the calculated vacuum-aligned VBE as a function of  $\epsilon$  for each of the energy favored terminations of the phase diagrams in Figure 3. The computed VBEs for the (001) and (110) facets are systematically below -5 eV, and practically independent of the applied strain. Conversely, the VBE of the (111) facets tends to increase with surface compression, the only exception being the *LMO-rec* termination whose VBE remains effectively constant regardless of the applied strain. Apart from the *LiO* termination, the VBE for all of the (111) terminations turns out to be above -4.0 eV for  $\epsilon \lesssim -3\%$ , indicative of a strongly enhanced reduction energy drive by comparison to the (110) and (001) facets ( $\text{VBE} < 5 \text{ eV}$ ), even in the presence of non-stoichiometry.

As seen in Figure 4c, the VBEs of the *Li-rich* and *Li-rich2* terminations of the (111) surface are the highest regardless of the strain applied. These results suggest that in Li-rich conditions (Figure 3), as favored by strongly concentrated electrolytes, the energetically favored, Li-terminated (111) surfaces should be robustly reducing, which may promote *zero-voltage* reactions with the electrolyte. This result is in qualitative agreement with earlier computational results on Li-rich (111) surfaces of spinel  $\text{Li}_7\text{Ti}_5\text{O}_{12}$ .<sup>64</sup> The present simulations extend these earlier considerations by showing how the reduction energy drive for Li-terminated (111) surfaces of spinel  $\text{LiMn}_2\text{O}_4$  can be further modulated by strain, with VBE change-rates as large as  $\approx +0.2 \text{ eV}$  for 1% compression/expansion (*Li-rich2* in Figure 4c). The results in Figures S22-23 indicate that the calculated CBE for the semiconducting, non-stoichiometric  $\text{LiMn}_2\text{O}_4$  surfaces show a rate of change with  $\epsilon$  that is comparable to what observed in Fig. 4d-f for the VBEs. Thus, the calculated dependence of the systems' band-gap on the applied strain turns out to be rather weak.

In conjunction with impressive advances in the controlled preparation of both epitaxial metal-oxide thin-films<sup>17,18,36,38</sup> and core-shell nanostructures,<sup>65,66</sup> the strong sensitivity to strain of the VBE and CBE (thence redox chemistry drive) for the stoichiometric and non-stoichiometric  $\text{LiMn}_2\text{O}_4$  surfaces (Figures 2, 4 and S22-23) motivates further research in strained  $\text{LiMn}_2\text{O}_4$  films and zero-voltage formation of CEI precursors therein. The same dependence of the VBE and CBE of

LiMn<sub>2</sub>O<sub>4</sub> surfaces on both strain and lithiation suggests also interesting opportunities in the development of strain- and lithiation-tailored LiMn<sub>2</sub>O<sub>4</sub> films for photo-catalytic applications.<sup>3,24,25</sup> We believe the calculated results and trends provide useful guidelines to prompt research in both of these directions.



**Figure 4.** Vacuum-aligned VBEs (a-c) and atom-resolved average magnetic moments with standard deviation (d-f) for the energy-favored, stoichiometric and non-stoichiometric terminations of the (001) (a,d), (110) (b,e) and (111) (c,f) LiMn<sub>2</sub>O<sub>4</sub> surfaces as a function of bi-axial strain ( $\epsilon$ ) in FM ordering.

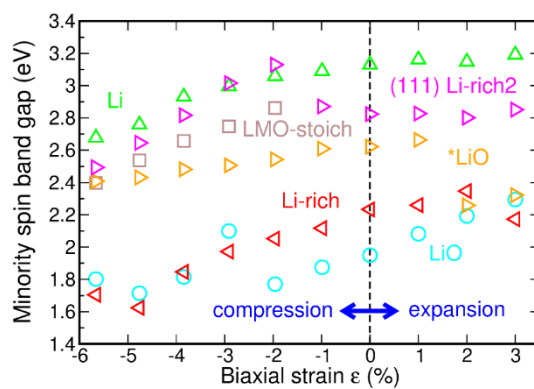
Turning to the magnetic properties of non-stoichiometric LiMn<sub>2</sub>O<sub>4</sub> surfaces, the results in Figure 4d-f indicate that compressive (tensile) strain leads to a decrease (increase) of the atomic magnetic moment for both low-spin Mn<sup>+4</sup> and high-spin Mn<sup>+3</sup> atoms also in the presence of non-stoichiometry. This trend is found consistently for all the (001), (110) and (111) orientations of the non-stoichiometric LiMn<sub>2</sub>O<sub>4</sub> films. We find the computed *average* values to be very weakly

dependent on the given surface termination, indicative of a non-immediate role for the *surface* Li-content in tuning the local magnetic properties of  $\text{LiMn}_2\text{O}_4$ . As for the stoichiometric models (Figure 2), the magnetic response of the O atoms to the application of strain is opposite to that of the Mn-atoms, leading to an overall strain-independent total magnetic moment for the simulated FM slabs. Notably, and in contrast with the result for the stoichiometric films (Fig. 2c), the simulations of the non-stoichiometric slabs reveal a non-negligible layer-dependence for the response of the atomic magnetic moments to the applied strain, which in turn generates an increased standard deviation for the calculated atomic moments in Fig. 4e-f. As detailed in Section SI-12 for the (111) *Li-rich2* slab (Figs. S25-27), such a response manifests in layer-dependent, local relaxed structures and oxidation states for specific subsets of atoms that are intermediate between the standard “+3” ( $\sim 3.9 \mu_B$ ) and “+4” ( $\sim 3.1 \mu_B$ ) results for bulk  $\text{LiMn}_2\text{O}_4$  and its stoichiometric surfaces in Figs. 1-2. As evident across Figs. 4d-f, the inhomogeneity of the atomic response to strain appears to increase going from the (001) film to the (110) and (111) ones, and to be enhanced by Li-termination. Overall, these results indicate that although the surface Li-content does not significantly change the average atomic magnetic moments of the film, it does enhance the (atomic and layer) inhomogeneity of its response to the applied strain.

Also in the presence of non-stoichiometry, all the [(110) and (111)-*Li-rich2*] metallic surfaces of  $\text{LiMn}_2\text{O}_4$  turn out to be half-metallic, with minority-spin band gaps strongly dependent on the applied strain (Figure 5). As per results in Figure S22, none of the (001) surface termination results in (half-)metallic solutions, within FM ordering. We find compressive ( $\epsilon < 0$ ) and tensile ( $\epsilon > 0$ ) strain to generally decrease and increase the minority spin band-gaps, respectively, albeit with exceptions such as the (111) *Li-rich2* and the (110) *\*LiO*, *LiO* and *Li-rich* terminations. Even the smallest minority-spin band-gap calculated [always larger than 1.4 eV for (110) *Li-rich* and  $\epsilon \lesssim -5\%$ ] turns out to be substantially larger ( $>30\%$ ) than for bulk FM (0.71 eV) or AFM (1.09 eV)  $\text{LiMn}_2\text{O}_4$  at the same level of theory.<sup>31</sup> These results indicate that, even in the presence of

substantial non-stoichiometry, strain in  $\text{LiMn}_2\text{O}_4$  thin-films can yield energy-favored (Figure S5), robust half-metallicity with minority spin band-gaps beyond the bulk value. These findings in turn point to the possibility of strain-mediated strategies to introduce markedly spin-dependent electron-transport properties in  $\text{LiMn}_2\text{O}_4$  films, likely to affect both the surface electrochemistry and the accumulation of spin-polarized, surface excess charge.<sup>27</sup>

The persistence of half-metallic states in the non-stoichiometric (110) and (111)  $\text{LiMn}_2\text{O}_4$  films indicates this property is rather robust with respect to (surface) compositional changes and, potentially, short-range disorder as recently observed at room-temperature for lithium-free, sub-stoichiometric Mn-oxides.<sup>27</sup> Given the well-known fragility of ferromagnetic half-metallic oxides to compositional changes and disorder,<sup>59,67-70</sup> the present results point to strained  $\text{LiMn}_2\text{O}_4$  films as a potential alternative system for spin-filtering applications that require robust ferromagnetism and half-metallicity. The absence of rare-earth metals in  $\text{LiMn}_2\text{O}_4$ , in contrast to state of the art ferromagnetic half-metallic oxides,<sup>59,67-70</sup> suggests further potential benefits in terms of sustainability,<sup>28</sup> thence motivation for further research into this subject.



**Figure 5.** Calculated minority-spin band-gap for the half-metallic (111) *Li-rich2* and (110) terminations of  $\text{LiMn}_2\text{O}_4$  as a function of bi-axial strain ( $\epsilon$ ). The (110) *LMO-stoich* termination becomes semiconducting for  $\epsilon > -2\%$ .

#### 4. CONCLUSIONS

DFT+(U-J) simulations of the energy favored, stoichiometric and non-stoichiometric  $\text{LiMn}_2\text{O}_4$  surfaces for different FM and AFM ordering in the presence of bi-axial strain reveal a marked (up to over 1 eV) increase in the reduction energy drive of the (111) terminations upon surface compression. This response could be further explored towards the design of new strategies to zero-voltage CEI-precursors for  $\text{LiMn}_2\text{O}_4$  LIB-cathodes as well as strain-mediated engineering of  $\text{LiMn}_2\text{O}_4$  band-edges for photo-electro-catalytic applications. The simulations indicate that, regardless of the FM or AFM ordering, the magnetic moment of the Mn-atoms increases (decrease) with application of tensile (compressive) strain. The simulations uncover a compensation mechanism whereby strain induces opposite changes in the magnetic moment of the Mn- and O-atoms, leading to an overall constant magnetic moment for FM slabs. This mechanism is observed in each of the systems studied apart from the AFM (001) Li-terminated surface, which indicates weak dependence on the crystallographic orientation of the film and its non-stoichiometry. These results are not affected by the specific method used to integrate the spin-density around atoms, which suggests the effect should be physical. Notably, several stoichiometric and non-stoichiometric (110)  $\text{LiMn}_2\text{O}_4$  surfaces, and one non-stoichiometric (111) surface, turn out to be both ferromagnetic and half-metallic with a minority-spin band-gaps strongly sensitive to strain and up to over 2 eV (~200%) larger than for bulk  $\text{LiMn}_2\text{O}_4$ , even in the absence of strain. Such values of minority spin band-gap are comparable with state of the art half-metallic ferromagnets based on oxides of rare earth metals. This in turn suggests markedly spin-dependent electron-transport properties that may affect also the electro-chemical and electro-catalytic reactions-mechanisms of the systems. The strong resilience of the calculated ferromagnetic half-metallic states to compositional changes (non-stoichiometry) suggests it may be rewarding to further explore the potential of strained  $\text{LiMn}_2\text{O}_4$ (110) thin-films for sustainable spintronics applications, starting from, but not limited to, spin-filtering and spin-storage as recently measured for lithium-free Mn-oxides.<sup>27</sup>

## Associated Content.

### Supporting Information

The Supporting Information, containing supplementary methods and results, is available free of charge at XXXX

Computational details for bulk  $\text{LiMn}_2\text{O}_4$  calculations (SI-1); Stability of bulk  $\text{LiMn}_2\text{O}_4$  (SI-2); Bulk  $\text{LiMn}_2\text{O}_4$  response to bi-axial strain (SI-3);  $\text{LiMn}_2\text{O}_4(111)$  inverse spinel reconstruction (SI-4); Symmetry restrictions in the simulation of the  $\text{LiMn}_2\text{O}_4$  slabs (SI-5); Supplementary results for the relative energy, electronic and magnetic properties of the stoichiometric  $\text{LiMn}_2\text{O}_4$  surfaces (SI-6); Spin-density integration to compute atomic magnetic moments (SI-7); Thermodynamic stability of  $\text{LiMn}_2\text{O}_4$  surfaces: Theory (SI-8); Models of the non-stoichiometric  $\text{LiMn}_2\text{O}_4$  surfaces (SI-9); Thermodynamic stability of non-stoichiometric  $\text{LiMn}_2\text{O}_4$  surfaces: Results (SI-10); Strain-dependence of the VB and CB edges for the non-stoichiometric  $\text{LiMn}_2\text{O}_4$  surfaces (SI-11); Supplementary results for the magnetic properties of non-stoichiometric  $\text{LiMn}_2\text{O}_4$  surfaces (SI-12); Bi-axial strain (epitaxial lattice misfit): definitions (SI-13).

**Author Contributions.** GT developed the original research concept that was eventually expanded in collaboration with IS. Both authors analyzed jointly the results of the DFT (hybrid DFT) simulations that were executed by IS (GT). The manuscript was jointly written by both authors.

**Notes.** The authors declare no competing financial interest.

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