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Thermodynamics and Electronic Structure of Earth-Abundant Materials for Next
Generation Li Batteries from First Principles

by

Ronald Linghin Kam

A dissertation submitted in partial satisfaction of the

requirements for the degree of

Doctor of Philosophy

in

Materials Science and Engineering

in the

Graduate Division

of the

University of California, Berkeley

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Professor Gerbrand Ceder, Chair

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Ronald Linghin Kam

Abstract

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in Materials Science and Engineering

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Professor Gerbrand Ceder, Chair

The demand for battery energy storage is rapidly growing, necessitating the development of novel battery chemistries that are affordable, utilize earth-abundant metals, and can deliver high energy density with long cycling stability. Promising avenues of research to achieve these goals include the development of solid-state electrolytes and novel cathode materials. The discovery and optimization of novel candidate phases can be accelerated through first-principles calculations to rationalize the atomic structure, phase diagrams, and other relevant properties, without empirical parameters. In our work, we investigate the phase stability and electronic structure of sulfide superionic conductor electrolytes and Mn-rich rock-salt oxide cathodes from first-principles calculations. Although the chemical nature of these materials is distinct, we are able to harness similar statistical thermodynamics approaches to model the phase stability. Specifically, these sulfides within the Li-P-S (LPS) composition space and Mn-rich oxides (Li-Mn-Ti-O, or LMTO) are crystalline ionic materials exhibiting configurational disorder, which we capture by using lattice model methods, namely the cluster expansion (CE) coupled with Monte Carlo (MC) sampling. We find that accounting for the vibrational free energy contributions within the harmonic phonon approximation is also essential for accurate predictions of the LPS phases.

The calculations of configurational and vibrational contributions to the free energy require accurate electronic structure methods to precisely evaluate the possible energy states. We harness density-functional theory (DFT) to calculate these quantities and train surrogate CE models. However, the LPS conductors and LMTO cathodes exhibit physical complexities that are non-trivial to treat within semi-local DFT exchange-correlation functionals. Specifically, the LPS conductors contain relatively long-range dispersion-type interactions within the sulfur (S) sublattice, which are not accurately captured within the generalized gradient approximation (GGA), but can be reasonably described within more recently developed meta-GGAs such as r^2 SCAN. The LMTO phases exhibit correlated and localized

3d electronic states, Jahn-Teller (JT) distortions, and antiferromagnetism of Mn^{3+} , leading to the failures of GGA and meta-GGA approaches to predict the correct ground states, a deficiency primarily attributed to the self-interaction error (SIE) that is inherent to these functionals. Instead, DFT methods that more precisely correct the SIE, such as hybrid-GGA and GGA with non-empirical Hubbard corrections, are needed to achieve reasonable ground state prediction of Mn^{3+} -rich compositions such as LiMnO_2 . We unveil the subtle interplay between the atomic and orbital ordering, magnetism, and degree of electronic localization/hybridization that determines the phase stability of LiMnO_2 .

The thorough benchmarking and application of DFT methods enable us to calculate the relevant phase diagrams of LPS superionic conductors and LMTO rock-salt cathodes with reasonable accuracy, recovering and rationalizing experimentally observed trends. Within the LPS phase diagram, we predict the experimentally known polymorphic phase transitions among the Li_3PS_4 and Li_7PS_6 phases, the metastability of $\text{Li}_7\text{P}_3\text{S}_{11}$ at all temperatures, and quantify the free energy differences between phases. We also clarify the details of the Li sublattices within specific LPS superionic conductors, which we find to be crucial for deriving physically accurate CE lattice models.

In the LMTO system, we predict the order-disorder transition temperatures (T_{disord}) as a function of composition to rationalize the thermodynamic accessibility of the disordered rock-salt (DRX) phase, a promising cathode material. Importantly, we predict the LMTO phase diagram to be eutectoid-like, in which the T_{disord} decreases as off-stoichiometry is introduced to the end-point compositions, which is confirmed from X-ray diffraction (XRD) experiments. Our LMTO phase diagram reveals that DRX is stable over a significant composition range at relatively low temperatures of 800 – 900 °C, significantly lower than the conventional synthesis temperatures (> 1000 °C), offering a route to optimize particle morphology and rate capability. We also elucidate the importance of Ti doping towards stabilizing DRX at synthetically accessible temperatures.

Contents

Contents	i
List of Figures	iii
List of Tables	x
1 Introduction	1
2 Thermodynamics from First-Principles	5
2.1 Statistical thermodynamics	5
2.2 Configurational disorder and cluster expansions	7
2.3 Phonons	12
3 Electronic Structure Theory	14
3.1 Density-functional theory (DFT)	14
3.2 Linear response DFT and DFPT	22
3.3 <i>GW</i>	24
4 Phase Stability of Li-P-S Superionic Conductors	26
4.1 Introduction	26
4.2 Phase stability in the $\text{Li}_2\text{S-P}_2\text{S}_5$ system	29
4.3 Li_3PS_4 polymorphs	31
4.4 Li_7PS_6 polymorphs	42
4.5 $\text{Li}_7\text{P}_3\text{S}_{11}$	44
4.6 Discussion	47
4.7 Conclusion	51
4.8 Methods	51
4.9 Appendix	53
5 Phase Stability and Electronic Structure of the LiMnO_2 Polymorphs	55
5.1 Introduction	55
5.2 Methods	58
5.3 Phase stability	60

5.4	Self-consistent Hubbard parameters	64
5.5	Electronic structure	68
5.6	Discussion	72
5.7	Implications on other LiMO_2 compositions	80
5.8	Conclusion	82
5.9	Appendix	83
6	Phase Diagram of Li-Mn-Ti-O Rock-Salt Phases	90
6.1	Introduction	90
6.2	LMTO phase diagram	94
6.3	Phase stability and structural distortions within Li-excess phases	101
6.4	Discussion	104
6.5	Conclusion	110
6.6	Methods	110
6.7	Appendix	113
7	Conclusion and Outlook	122
	Bibliography	124

List of Figures

1.1	Schematic of a Li battery cell, reproduced from Ref. [1].	2
3.1	Schematic of the LDA, exact DFT, and LDA+ U correction energy as a function of electron count. Reproduced from Cococcioni et al [122].	22
4.1	Composition line and arrangements of PS_4 tetrahedral units in the Li_2S - P_2S_5 system. a) Location of Li_7PS_6 , Li_3PS_4 , and $\text{Li}_7\text{P}_3\text{S}_{11}$ on the composition line, labeled by the ratios of Li_2S to P_2S_5 . Arrangements of PS_4 and P_2S_7 units in b) γ - Li_3PS_4 , c) β - Li_3PS_4 , d) α - Li_3PS_4 , e) LT- Li_7PS_6 , f) HT- Li_7PS_6 , g) $\text{Li}_7\text{P}_3\text{S}_{11}$. Unit cell boxes are drawn for LT- Li_7PS_6 and HT- Li_7PS_6 to show their cubic and orthorhombic PS_4 arrangement, respectively.	27
4.2	Phase stability of the Li_2S - P_2S_5 pseudo-binary system. a) Phase diagram at 0 K, 700 K, and 1000 K. Solid lines denote the convex hull. Stable phases that are on the convex hull are marked with squares and labeled in green. Unstable phases are marked with gold stars and labeled in black. b) Free energy above hull for all phases from 0 to 1000 K.	30
4.3	Structure of β - Li_3PS_4 . a) (i) Unit cell with Li1 (8d) (green), Li2 (8d) (orange), Li3 (4c) (blue), and Li 4 (8d) (brown) sites. (ii) Splitting of Li1' (8d) (grey) to Li1 (8d) and Li4 (8d). (iii) Splitting of Li2' (4b) (grey) from square planar coordination to 5-fold coordinated Li2 (8d). b) Distributions of atomic relaxations in DFT starting from ideal ND and XRD refined structures. The extent of atomic relaxations are measured in normalized root mean squared (NRMS) atomic displacements. The dashed lines denote the 25, 50, 75 percentiles in the distributions.	32
4.4	Structures of the a) XRD ground state (XRD-GS) and b) ND ground state (ND-GS) of β - Li_3PS_4 . XRD-GS contains linear ordering of Li1 and Li2 atoms along [010] and [001], while the ND-GS has distorted, staggered chains along [010]. Phonon dispersions of the c) XRD-GS and (d) ND-GS. e) Visualizing an imaginary optical mode of XRD-GS at Γ , showing collective motion of Li2 atoms (orange). The blue and grey arrows indicate mode displacement directions. . . .	34
4.5	Li site fractional occupancies in β - Li_3PS_4 across temperature in MC simulations, for the a) XRD-refined lattice and b) ND-refined lattice.	35

- 4.6 Structure of α - Li_3PS_4 . a) The unit cell with Li1 (16h) (green), Li2 (8e) (red), and Li3 (4c) (blue) sites. The boxed region is shown in greater detail in b) to display the local Li coordination. Nearest Li1 and Li2 sites are face-sharing to form a connected Li channel along [010]. Two adjacent channels are connected by Li3 sites, which are edge-sharing with Li1. c) The ground state structure with monoclinic $\text{P}2_1/\text{c}$ symmetry. Li atoms occupy only Li1 sites, forming distorted linear chains of Li along [010] and [001]. d) Li site fractional occupancies from MC simulations. 37
- 4.7 Free energy of α and β - Li_3PS_4 relative to γ - Li_3PS_4 . All experimentally reported phase transitions are observed when accounting for all free energy contributions (solid lines). $\gamma - \beta$ transition occurs at 370 K (523 – 573 K from exp.), $\beta - \alpha$ at 460 K (723 – 748 K from exp.), and $\alpha - \gamma$ at 420 K (533 K from exp upon cooling). Only the $\gamma - \beta$ transition is observed when including only vibrational entropy contributions (dotted lines). Shaded blue and orange regions indicate experimentally observed $\gamma - \beta$ and $\beta - \alpha$ phase transitions, respectively. 39
- 4.8 Phonon density of states. a) Total density of states (TDOS) for each Li_3PS_4 polymorph. Projected density of states (PDOS) onto Li, P, and S atoms for b) β , c) γ and d) α - Li_3PS_4 as a function of frequency and thermal energy temperature ($T = hf/k_B$), normalized per unit cell of β - Li_3PS_4 (4 formula units). γ - Li_3PS_4 contains smaller DOS at frequencies of 1-2 THz and 6 THz. The region of 1-2 THz is dominated by S modes. At 5-8 THz, γ has much larger density of S modes compared to Li, while in α and β there are equal contributions of each. 40
- 4.9 Orbital resolved electronic density of states (eDOS) of γ , β , and α - Li_3PS_4 ground state structures. Energies are referenced to the Fermi level (E_F). All phases exhibit a valence band manifold consisting of mainly S-3p states, and a lower energy core band manifold composed of hybridized S-3p and P-3p states. γ - Li_3PS_4 has a larger energy gap (ΔE) between valence and core band manifolds (1.6 eV) compared to α and β (0.8 and 1.0 eV), as well as a sharper eDOS peak in the core manifold. 41
- 4.10 Structure of HT- Li_7PS_6 . a) The unit cell (F-43m) with Li1 (48h) (green) sites that are corner-sharing with PS_4 , and Li2 (48h) (orange) sites that are edge-sharing with PS_4 . The boxed region containing a single cage-like Li substructure is shown in greater detail in b), which displays the local Li site coordination. Dotted lines connect face-sharing Li atoms. c) Violin plots displaying distributions of normalized root mean squared (NRMS) atomic displacements of DFT relaxed configurations from ND and XRD refinements. Dashed lines denote division between data quartiles. d) Ground state structure of HT- Li_7PS_6 , containing 6 occupied Li2 (48h) sites (orange). 43
- 4.11 HT- Li_7PS_6 Li site occupancy fractions across temperature. The reported experimental occupancies (triangles) were measured with ND on $\text{Li}_6\text{PS}_5\text{Cl}$ at 300 K, and are scaled by 7/6 to account for the different Li stoichiometry, compared to Li_7PS_6 44

4.12	Structure of LT-Li ₇ PS ₆ . a) The ground state structure identified from AIMD simulations. PS ₄ units relax slightly away from a parallel arrangement, contributing to a slight monoclinic distortion, with unit cell angles: $(\alpha, \beta, \gamma) = (90.0, 91.0, 90.0)$. b) Histogram of energies above ground state for structures sampled along the AIMD trajectory. Reported energies are calculated from ionic relaxations using the PBE functional.	45
4.13	Free energy of HT-Li ₇ PS ₆ relative to LT-Li ₇ PS ₆ . Phase transition from LT to HT is predicted at 280 K, compared to 483 K from experiment.	45
4.14	Disordered unit cell of Li ₇ P ₃ S ₁₁ with 7 distinct Li sites identified from XRD (green) and 8 distinct sites identified from AIMD simulations (orange).	46
4.15	Configurational entropy in the disordered superionic conductors α -Li ₃ PS ₄ , β -Li ₃ PS ₄ , HT-Li ₇ PS ₆ , and Li ₇ P ₃ S ₁₁ phases, normalized per Li atom.	47
4.16	Comparing Li site energies in α and β -Li ₃ PS ₄ polymorphs. a) ECI energies corresponding to single-site functions in the CE (J_{ECI} , denoted by triangles), and ECI energies normalized by site multiplicity ($\hat{J}_{ECI}$, denoted by stars). In β , the sites are Li1 8d, Li2 8d, Li3 4c, and Li4 8d. Positive values correspond to an increase in energy from Li occupying a site. In α , the sites are Li1 16h, Li2 8e, and Li3 4c. b) Standard deviation of $\hat{J}_{ECI}$	50
4.17	CE training and cross-validation errors.	53
4.18	ECI of α - and β -Li ₃ PS ₄ CE models.	54
5.1	Structures of the LiMnO ₂ phases that are examined in this study. The majority (up, purple) and minority (down, blue) spin channels of Mn are distinguished to display the ground state AFM orderings that we identify. The long Mn-O bonds (JT axis) are shown in orange and Li-O bonds are omitted for clarity. The space groups are labeled in parentheses. The spinel phase (b) is specifically the lithiated spinel (Li ₂ Mn ₂ O ₄ in spinel notation). In ϵ -LiMnO ₂ (f), all JT axes are aligned perpendicular to the page and are not visible in the figure.	56
5.2	DFT energy of LiMnO ₂ phases relative to ortho-LiMnO ₂ in the a) FM and b) AFM spin configurations, and c) energy differences between the AFM and FM spin orderings (ΔE_{AFM-FM}). Energies are computed with PBEsol + U ($U = 3.9$ eV), r ² SCAN, and r ² SCAN+ U ($U = 1.8$ eV) in VASP.	61
5.3	DFT energy of the LiMnO ₂ polymorphs relative to ortho, in their respective ground state AFM spin configurations. The functionals used are HSE06, PBEsol (GGA) with self-consistently (sc) determined U (PBEsol+ U_{sc}), PBEsol+($U + V$) _{sc} , and PBEsol with averaged (avg) $U = 6$ eV and $V = 0.6$ eV.	63
5.4	Total free energy (F) relative to ortho-LiMnO ₂ as a function of temperature. F(T) is the sum of the vibrational free energy and DFT energy. Harmonic phonon calculations are performed within PBEsol + U ($U = 3.9$ eV) and DFT energies are computed within PBEsol + ($U + V$) _{sc}	64

5.5	Correlating self-consistent HPs from PBEsol + $(U + V)_{\text{sc}}$ with the local electronic structure and bonding environments. Plots of a) Hubbard U with Mn magnetic moment and b) V with Mn-O bond length. All magnetic moments and bond lengths are calculated from the self-consistent HPs. The values of HPs are distinguished by the noncollinear (orange crosses) and collinear (green squares) JT distortions. Lines of best fit and R^2 values are shown.	67
5.6	Structure of the disordered layered phase and table of Hubbard U and magnetic moments corresponding to each labeled Mn, calculated within PBEsol + $(U + V)_{\text{sc}}$. Mn atoms are distinguished by their spins (blue for up-spin, and purple for down-spin). Green atoms - Li, red atoms - O.	68
5.7	Isosurfaces of the difference in charge density (ρ) between FM and AFM states of ortho-LiMnO ₂ ($\rho(\text{AFM}) - \rho(\text{FM})$) computed within PBEsol + $U + V$, visualized at two different crystal orientations as shown in the top panels. The yellow (blue) regions indicate areas of increased (decreased) ρ in the AFM structure. The bonds highlighted in orange correspond to the long bond (~ 2.3 Å) in the Jahn-Teller complex.	70
5.8	Projected density of states (pDOS) of ortho-LiMnO ₂ computed using a) PBEsol, b) PBEsol + U , c) PBEsol + $U + V$, d) PBEsol + $U_{\text{Mn,O}} + V$, e) HSE06, and f) r ² SCAN + U . Blue: Mn-3d, orange: O-2p, and grey: total DOS. Energies are referenced to E_{F}	71
5.9	Electronic band structure of the ND-refined AFM ortho-LiMnO ₂ structure, computed using a) PBEsol + U , b) GW (G_0W_0) starting from the PBEsol + U wave functions, and c) HSE06. The majority and minority spin channels are degenerate. In b), the band energies are referenced to the E_{F} calculated from PBEsol + U and the PBEsol + U band structure is shown in light grey to highlight the GW self-energy corrections. Marked squares in b) and c) indicate the points where the band energies are computed and the lines are linear interpolations between them.	73
5.10	Simulated XRD (Cu K- α radiation) patterns of LiMnO ₂ and Li ₂ MnO ₃ phases. Each structure is relaxed within HSE06 and the identified space group of the final structure is shown in parentheses.	76
5.11	Structures of AFM layered LiMnO ₂ with a) zig-zag (P2 ₁ /c) and b) collinear (C2/m) ordering of JT axes. Only one Mn layer is shown for clarity. The JT axes are highlighted in orange. Blue - Mn (up spin), purple - Mn (down spin), and red - O.	79
5.12	DFT energy of LiMO ₂ phases ($M = \text{Co, Cr, Ni, Fe}$) relative to the layered phase, calculated using PBEsol + U , r ² SCAN, and r ² SCAN + U with empirical U . All calculations use FM order, except for the LiCoO ₂ calculations which were nonmagnetic.	81
5.13	Comparison of computed energies of the LiMnO ₂ phases relative to orthorhombic LiMnO ₂ within PBEsol + U across a) VASP and b) QE (PWscf). Hubbard U is imposed on Mn-3d manifolds. Each calculation is a SCF calculation.	84

5.14	Plots of self-consistent Hubbard U and Mn magnetic moments within each LiMnO_2 phase, calculated using PBEsol + U_{sc} and PBEsol + $(U + V)_{sc}$. Lines of best fit and R^2 values are also displayed.	85
5.15	DFT energy of each LiMnO_2 phase (with AFM configuration) relative to the orthorhombic phase, within several DFT approximations.	87
5.16	Band structure of the experimentally refined ortho- LiMnO_2 structure computed within PBEsol.	88
5.17	Comparing the Mn magnetic moments computed using PBEsol with self-consistent (sc) HPs and averaged (avg) HPs.	89
5.18	Special quasi-random structure of LiMnO_2 relaxed with PBEsol + U . JT axes are labeled in orange. Purple: Mn, green: Li, red: O.	89
6.1	Composition and configuration space of the LMTO rock-salt phases. a) Pseudo-ternary $\text{LiMnO}_2 - \text{Li}_2\text{MnO}_3 - \text{Li}_2\text{TiO}_3$ composition space. Nominal TM oxidation states and changes in composition along the edge pseudo-binary lines are labeled. b) Unit cell of the FCC rock-salt lattice, with octahedral cation sites that can be occupied by Li^+ , Mn^{3+} , Mn^{4+} , or Ti^{4+}	92
6.2	DFT-computed formation energies at 0 K and Mn magnetic moments of the training set of LMTO rock-salt orderings. a) Formation energies of structures within the LMTO pseudo-ternary — specifically the lowest energies of each sampled composition. Green circles represent stable phases and squares represent configurations with energy above the convex hull. b) Histogram of absolute values of Mn magnetic moments ($ m_{\text{Mn}} $). The vertical line at $ m_{\text{Mn}} = 3.35 \mu_B$ denotes the threshold between Mn^{3+} and Mn^{4+} , with all Mn with $ m_{\text{Mn}} > 3.35 \mu_B$ assigned to be Mn^{3+} , while Mn with $ m_{\text{Mn}} < 3.35$ assigned as Mn^{4+} . Formation energies along the pseudo-binary c) $\text{LiMnO}_2 - \text{Li}_2\text{TiO}_3$ ($\text{Li}_{1+x}\text{Mn}_{1-3x}^{3+}\text{Ti}_{2x}^{4+}\text{O}_2$) and d) $\text{LiMnO}_2 - \text{Li}_2\text{MnO}_3$ ($\text{Li}_{1+x}\text{Mn}_{1-3x}^{3+}\text{Mn}_{2x}^{4+}\text{O}_2$) composition lines, where green squares are stable phases and orange lines are configurations above the convex hull. . . .	95
6.3	Temperature — composition phase diagrams of the pseudo-binary composition spaces of a) $\text{LiMnO}_2 - \text{Li}_2\text{TiO}_3$, b) $\text{LiMnO}_2 - \text{Li}_2\text{MnO}_3$, and c) $\text{LiMnO}_2 - \text{Li}_2\text{Mn}_{0.5}\text{Ti}_{0.5}\text{O}_3$, calculated from MC simulations (black lines). Gold stars represent T_{disord} determined from <i>in situ</i> XRD experiments, which were performed for select compositions along the $\text{LiMnO}_2 - \text{Li}_2\text{TiO}_3$ and $\text{LiMnO}_2 - \text{Li}_2\text{MnO}_3$ pseudo-binaries only. . . .	97
6.4	<i>Ex situ</i> XRD patterns of samples quenched from various temperatures. a) $\text{Li}_{1.05}\text{Mn}_{0.85}\text{Ti}_{0.1}\text{O}_2$, b) $\text{Li}_{1.1}\text{Mn}_{0.7}\text{Ti}_{0.2}\text{O}_2$, c) $\text{Li}_{1.25}\text{Mn}_{0.25}\text{Ti}_{0.5}\text{O}_2$, and d) $\text{Li}_{1.3}\text{Mn}_{0.1}\text{Ti}_{0.6}\text{O}_2$, each quenched from temperatures above (red) and below (black) their respective T_{disord}	99
6.5	<i>Ex situ</i> XRD patterns of compositions $\text{Li}_{1.05}\text{Mn}_{0.95}\text{O}_2$, $\text{Li}_{1.1}\text{Mn}_{0.9}\text{O}_2$, and $\text{Li}_{1.25}\text{Mn}_{0.75}\text{O}_2$, each quenched from 1100 °C.	100
6.6	Energy above the hull (E_{hull}) of Li-excess orthorhombic (ortho), layered, spinel, and γ phases at the a) $\text{Li}_{1.0625}\text{Mn}_{0.9375}\text{O}_2$ and b) $\text{Li}_{1.0625}\text{Mn}_{0.8125}\text{Ti}_{0.125}\text{O}_2$, c) $\text{Li}_{1.125}\text{Mn}_{0.875}\text{O}_2$, and d) $\text{Li}_{1.125}\text{Mn}_{0.625}\text{Ti}_{0.25}\text{O}_2$ compositions, computed from DFT at $T = 0$ K.	102

6.7	Histograms of TM–O bond lengths in Li-excess ortho $\text{Li}_{1.125}\text{Mn}_{0.875}\text{O}_2$ and Ti-doped $\text{Li}_{1.125}\text{Mn}_{0.625}\text{Ti}_{0.25}\text{O}_2$ structures. a) Mn^{3+} -O bond lengths within structures containing Ti-doping and no Ti, b) Ti^{4+} -O and Mn^{4+} -O bond lengths. Dashed lines mark the Mn^{3+} -O bond lengths within ortho LiMnO_2	103
6.8	TiO_6 octahedron in a relaxed ortho $\text{Li}_{1.125}\text{Mn}_{0.625}\text{Ti}_{0.25}\text{O}_2$ structure with labeled bond lengths in Å.	104
6.9	Pseudo-ternary phase diagram of $\text{LiMnO}_2 - \text{Li}_2\text{MnO}_3 - \text{Li}_2\text{TiO}_3$ at 800, 900, 1000, and 1100 °C. The two-phase and three-phase regions are labeled as 2p and 3p, respectively. Black points are obtained from the calculated pseudo-binary phase diagrams (Figure 6.3) and the lines are interpolations between them. Gray shaded regions are DRX, green lines represent layered $\text{Li}_2\text{D}^{4+}\text{O}_3$, and the orange line in c) denotes the Li-excess layered phase observed in experiment, which our calculations predict to be metastable.	105
6.10	Free energies (F) and Mn disproportionation of DRX LiMnO_2 as a function of temperature in MC simulations using a 5-component CE model containing Li^+ , Ti^{4+} , Mn^{2+} , Mn^{3+} , and Mn^{4+} . a) F relative to ortho- LiMnO_2 ($F - F_{\text{ortho}}$) computed within the grand-canonical (GC) and canonical ensembles. GC allows for Mn disproportionation, while canonical maintains Mn in the +3 state only. Vertical line at 1280 °C marks where DRX intersects with ortho- LiMnO_2 , thus the T_{disord} . b) Fraction of Mn disproportionated in DRX LiMnO_2 within GCMC simulations.	109
6.11	CE-computed formation energies at 0 K of the training set of LMTO rock-salt orderings. a) Formation energies of considered structures within the LMTO pseudo-ternary. b) $\text{LiMnO}_2 - \text{Li}_2\text{TiO}_3$ ($\text{Li}_{1+x}\text{Mn}_{1-3x}^{3+}\text{Ti}_{2x}^{4+}\text{O}_2$) and c) $\text{LiMnO}_2 - \text{Li}_2\text{MnO}_3$ ($\text{Li}_{1+x}\text{Mn}_{1-3x}^{3+}\text{Mn}_{2x}^{4+}\text{O}_2$) composition lines.	114
6.12	Free energy and internal energy of layered $\text{Li}_2\text{Mn}_{0.5}^{4+}\text{Ti}_{0.5}^{4+}\text{O}_3$ relative to its minimum energy, computed from canonical MC simulations.	115
6.13	Average energies relative to the ground state energy of the ortho LiMnO_2 , layered Li_2TiO_3 , and layered Li_2MnO_3 phases, calculated using canonical MC heating simulations.	115
6.14	XRD patterns of compositions a) $\text{Li}_{1.05}\text{Mn}_{0.85}\text{Ti}_{0.1}\text{O}_2$, and b) $\text{Li}_{1.1}\text{Mn}_{0.7}\text{Ti}_{0.2}\text{O}_2$, quenched from 1000 °C and 900 °C, respectively. They are refined based on the rock salt structure. The lattice parameter (a) and weighted profile R factor (R_{wp}) are shown in the figures.	116
6.15	XRD patterns of compositions a) $\text{Li}_{1.25}\text{Mn}_{0.25}\text{Ti}_{0.5}\text{O}_2$, and b) $\text{Li}_{1.3}\text{Mn}_{0.1}\text{Ti}_{0.6}\text{O}_2$, quenched from 700 °C and 750 °C, respectively. They are refined based on the rock salt structure. The lattice parameter (a) and weighted profile R factor (R_{wp}) are shown in the figures.	117

6.16	XRD pattern of the $\text{Li}_{1.05}\text{Mn}_{0.95}\text{O}_2$ sample collected at 1100 °C during the <i>in situ</i> experiment. No orthorhombic/monoclinic LiMnO_2 or layered Li_2MnO_3 phases are detected, confirming that the material is phase-pure DRX at this temperature. The additional peaks arise from the alumina sample holder and from reactions between excess Li_2CO_3 and the holder at high temperature.	117
6.17	<i>Ex situ</i> XRD pattern of $\text{Li}_{1.05}\text{Mn}_{0.95}\text{O}_2$ sample quenched from 1000 °C. Layered LiMnO_2 , orthorhombic LiMnO_2 and DRX phases are observed.	118
6.18	Comparison of CE and DFT energies of LiMnO_2 phases relative to ortho LiMnO_2 . These phases were previously analyzed in Chapter 5.3 and Ref. [259].	118
6.19	Free energy of layered $\text{Li}_{1.05}\text{Mn}_{0.85}^{3+}\text{Mn}_{0.1}^{4+}\text{O}_2$ relative to the convex hull, computed from canonical MC simulations.	119
6.20	Effective cluster interactions (ECI) of the quaternary CE model. Black lines denote the division between pair, triplet, and quadruplet interactions (from left to right).	119
6.21	Formation energy landscape of the layered $\text{Li}_2\text{Ti}_{1-x}\text{Mn}_x\text{O}_3$ ($\text{Li}_2\text{D}^{4+}\text{O}_3$) space at varying T , computed from canonical MC simulations.	120
6.22	Optimizing the ℓ_1 (α) and ℓ_2 (β) regularization hyperparameters within the Elastic Net regression approach. For each α , the cross-validation (CV) and training set RMSE is plotted as a function of β . The black line denotes the chosen model, with $\alpha = 1e-4$ and $\beta = 3.55e-3$. Blue shaded regions denote the standard deviation of the 5-fold CV trials.	121

List of Tables

4.1	Phase stability of Li_3PS_4 polymorphs at 0 K. Energies relative to $\gamma\text{-Li}_3\text{PS}_4$ [meV/atom] are calculated using PBE and r ² SCAN functionals, with and without the zero point vibrational energy. Zero point vibrational energy is calculated using the frozen phonon method with PBE.	38
5.1	Hubbard on-site U (Mn-3d), inter-site V (Mn3d – O 2p) parameters, and JT bond ratios ($\frac{\text{avg. long}}{\text{avg. short}}$) in the LiMnO_2 phases. Hubbard parameters (in units of eV) are self-consistently calculated using DFPT. Only the distinct values of each property are listed. V of the short (1.9-2.0 Å) and long (2.2-2.3 Å) Mn-O bonds are shown in separate rows. Reference values of the JT bond ratios from experimentally refined structures are listed.	65
5.2	Magnetic moment of Mn and band gap of ortho- LiMnO_2 computed from self-consistent field calculations using various DFT functionals (Quantum ESPRESSO). AFM order is used, unless otherwise stated.	69
5.3	Phonon entropy [$k_B/\text{f.u.}$] of the LiMnO_2 phases as a function of temperature.	77
5.4	Comparing the properties of layered LiMnO_2 with collinear and zig-zag orderings of JT axes – self-consistent Hubbard parameters, Mn moments, and JT bond ratio ($\frac{\text{long}}{\text{avg. short}}$) within PBEsol + $(U + V)_{\text{sc}}$	79
5.5	Calculation details of structural relaxations performed within VASP and QE. The Hubbard U , if applied, is imposed on the Mn-3d manifold. All calculations were performed using VASP except for PBEsol+ U + V (QE).	83
5.6	Self-consistent Hubbard U , Mn magnetic moments, and JT bond ratios of the LiMnO_2 phases within r ² SCAN and PBEsol, calculated using ONCV pseudopotentials.	86
5.7	Hubbard on-site U_{Mn} , U_{O} , and inter-site V (Mn3d - O2p) parameters in orthorhombic LiMnO_2 , self-consistently calculated using DFPT at the experimentally refined configuration and GGA+ U + V relaxed configuration (also shown in the main text Table I). Only the distinct values are listed. V of the short (1.9-2.0 Å) and long (2.2-2.3 Å) Mn-O bonds are shown in separate rows.	87
6.1	DFT convergence criteria and plane wave energy cutoffs.	113

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Chapter 1

Introduction

Lithium-ion (Li) batteries have become ubiquitous throughout society, as they power the vast majority of our personal electronics and electric vehicles [1, 2]. The continued development and deployment of novel energy storage technologies is vital towards combating rising CO₂ emissions and climate change [2, 3]. The deployment of energy storage on a grid scale enables the expansion of intermittent renewable energy sources such as wind and solar power [3]. Furthermore, the electrification of transportation significantly contributes to decarbonization, especially if the electricity is generated from renewable sources. Falling costs in Li battery manufacturing means that it has become economically feasible to install energy storage on increasingly large scales.

The demand for Li batteries and other energy storage technologies has recently surpassed 1 TWh/year and is projected to multiply swiftly in the next decades [2]. To meet this demand, we must develop technologies that only use cheap and earth-abundant elements in all components of the battery, to prevent potential materials supply chain bottlenecks [4, 5]. State of the art cathode materials with high energy density contain large fractions of nickel (Ni) and/or cobalt (Co) [6, 7, 8], which have relatively high cost and low abundance. This motivates our extensive investigation of cathode materials based on much more abundant TMs such as Mn and Ti.

Another important research area is to increase the cell energy density, which can in turn reduce cell manufacturing costs. A promising strategy is to develop solid-state batteries, which contain a solid electrolyte instead of a conventional organic liquid electrolyte [1, 9, 10]. The use of a solid electrolyte can potentially increase cell energy density by enabling the use of Li metal anodes, which have poor cycling stability within liquid electrolytes due to uncontrolled Li dendrite growth [9, 11]. Therefore, we also investigate superionic conducting materials, in which the Li mobility can be remarkably higher than in liquid electrolytes, making them promising candidates for solid-state electrolytes.

A Li battery cell is composed of three main components: the cathode, electrolyte, and

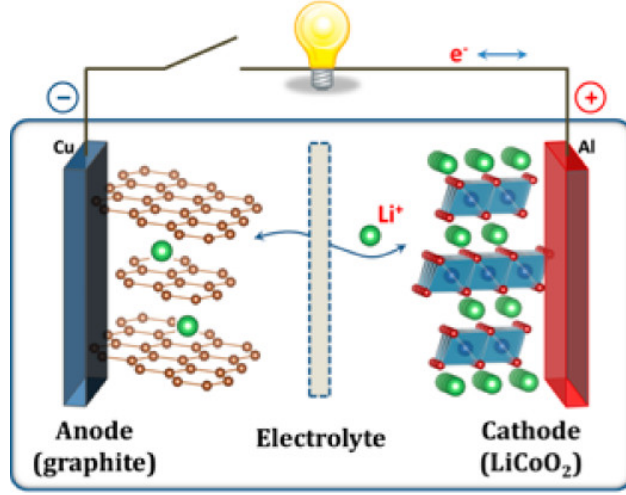


Figure 1.1: Schematic of a Li battery cell, reproduced from Ref. [1].

anode, a schematic of which is shown in Figure 1.1. The electrical potential energy in the cell arises from the difference in Li chemical potential (μ_{Li}) between the cathode and anode, which drives Li ions to transfer from anode to cathode on discharge [1, 12, 8]. The potential difference between the electrodes (V_{cell}) is determined by the Nernst equation

$$V_{\text{cell}} = -\frac{\mu_{\text{Li, cathode}} - \mu_{\text{Li, anode}}}{e} \quad (1.1)$$

while the cell energy is

$$E_{\text{cell}} = \int_{q_0}^q V_{\text{cell}} dq \quad (1.2)$$

where $q - q_0$ is the charge delivered. To charge the cell, an external load is applied to drive Li to transfer from cathode to anode.

During (dis)charge, Li diffuses through the electrolyte while electrons primarily travel through the external circuit, upon which electric work can be extracted. The electrons at electrode interfaces are also exposed to the electrolyte, leading to inevitable electrochemical reactions with the electrolyte solvent or salt species. Sometimes, these reactions are favorable, as exemplified by the well-known formation of a passivating solid-electrolyte interphase (SEI) film on the anode, which is essential for long cycling stability [13, 14, 15]. However, many other side reactions can cause significant damage to the electrodes and irreversibly consume the electrolyte, leading to energy fade.

Cathode materials can take the form of various TM oxide phases [1, 8, 16, 17]. Specifically, redox-active TM species are needed, which can accept/donate electrons through changing oxidation state, which charge compensates for the transfer of Li. The cell potential and

resulting cell energy is highly dependent on the TM redox couple and Li site energy, which largely dictate $\mu_{\text{Li, cathode}}$. Cathode materials must also remain structurally and chemically stable over thousands of Li (de)intercalation cycles to be commercially viable for personal devices and electric vehicles. Currently commercialized Li cathode materials are typically either close-packed layered oxides or phosphates with the olivine structure [7, 17, 18]. The layered phases are rock-salt type structures with alternating planes of Li and TM, usually with the formula LiMO_2 , where M can be a single TM or admixture of metals. Initially, layered LiCoO_2 was the first Li cathode material to be commercialized [7], but more recently Ni-rich LiMO_2 have become prominent due to their higher energy density [6, 17]. Olivine phases such as LiFePO_4 have become popular as well, partly due to Fe being lower in cost, though LiFePO_4 has significantly lower energy density compared to the layered LiMO_2 counterparts [18].

More recently, disordered rock-salt with Li-excess (DRX) phases have emerged as promising high energy density cathodes [19, 20, 21, 22, 23]. The DRX phase also possesses the close-packed rock-salt type structure, with the cations (nearly) randomly arranged on the cation sublattice. A favorable aspect of DRX is that they can utilize a variety of earth-abundant TMs, while the layered phases require the use of Ni and/or Co to maintain the layered ordering upon Li (de)intercalation. We will investigate the DRX phases in Chapter 6.

The commercialized Li battery electrolytes are usually composed of various organic solvents and inorganic Li salts [1, 14]. In the past two decades, there has been intense efforts to replace liquid electrolytes with solid-state electrolytes. Solid-state batteries are generally safer, as solid electrolytes are non-flammable ceramics [24, 25, 26]. They can also potentially enable the use of Li metal anodes, which would increase the cell energy density compared to conventional graphite anodes [9]. Solid-state batteries require the use of superionic conductors as the electrolytes, as they have high Li conductivity that can remarkably exceed conventional liquid electrolytes [25, 27]. There are many classes of superionic conductors, ranging from sulfides, oxides, and more recently (oxy)-halides, each with several possible crystal structures [24, 11, 27]. We will investigate the thermodynamics of sulfide superionic conductors in Chapter 4.

To investigate these Li superionic conductor and cathode phases, we harness first-principles calculations, which have significantly accelerated the development of Li batteries, as they can predict the atomic arrangements, phase diagrams, voltage profiles, kinetic properties, and electronic structure of battery materials with reasonable accuracy, insights which have complemented and/or guided experimental findings [28, 29, 12]. The utilization of electronic structure methods such as density-functional theory (DFT) has enabled precise calculations of materials properties only from knowledge of the atomic positions, without empirical fitting of parameters [30, 31]. DFT-based *ab initio* molecular dynamics (AIMD) simulations and Nudged Elastic Band (NEB) calculations have provided atomic-scale insight into the

ion transport mechanisms, timescales, and energy barriers [29, 12]. Recent advances in formalism, algorithms, and computational infrastructure have enabled DFT calculations to be performed in high-throughput, enabling the swift screening of candidate phases with favorable electrochemical properties and the construction of massive datasets of computed materials properties [31, 32, 33]. These datasets can in turn be utilized to train surrogate models such as cluster expansions (CE) [34, 35] and machine-learned potentials (MLPs) [36, 37, 38], which can be harnessed in Monte Carlo (MC) and molecular dynamics simulations, respectively, to simulate these materials at longer length and time scales.

The rest of this dissertation is organized as follows. In Chapter 2, the statistical thermodynamics theory used to study the phase stability of superionic conductors and cathodes is described. In Chapter 3, the electronic structure methods harnessed to investigate these materials are summarized. These theories and methods are applied towards understanding the thermodynamics and electronic structure of sulfide superionic conductors (Chapter 4) and Mn-rich cathode materials (Chapters 5 and 6). Through these studies, we derive novel understanding of these promising materials, which can guide future developments of sustainable and high-energy density Li batteries.

Chapter 2

Thermodynamics from First-Principles

From the basic tenets of thermodynamics, in conjunction with modern first-principles simulation methods, we can predict the bulk thermodynamic properties and phase diagrams of battery materials without empirical fitting [39]. Statistical mechanics principles are required to link the quantities derived from the quantum mechanical states of a material to its free energy, entropy, and other thermodynamic quantities. In this chapter, we will briefly review the formalism of statistical thermodynamics and the first-principles methodologies required to precisely evaluate the thermodynamic properties and phase stability of materials.

2.1 Statistical thermodynamics

Our aim is to accurately quantify the energetics of each material system as a function of temperature, composition, and/or other controlled variables. For a material at constant temperature T and pressure P , the minimized thermodynamic potential is the Gibb's free energy (G), which is a Legendre transform of the internal energy U ($G = U - TS + PV$) [40]. Within materials, the PV work term is relatively negligible, so the Helmholtz free energy F (Equation 2.1a) provides an accurate approximation to G . Specifically, F is the thermodynamic potential that is minimized at conditions of controlled T , number of particles (N), and volume (V) (i.e. the canonical ensemble), with its differential form stated in Equation 2.1b.

$$F = U - TS \tag{2.1a}$$

$$dF = -SdT + \mu dN \tag{2.1b}$$

For open systems in which the composition can fluctuate at constant T and V , the minimized thermodynamic potential is the grand potential free energy Ω (Equation 2.2a),

with its differential form written in Equation 2.2b.

$$\Omega = F - \mu N = U - TS - \mu N \quad (2.2a)$$

$$d\Omega = -SdT - Nd\mu \quad (2.2b)$$

Examples of grand-canonical systems include a battery cathode during cell discharging, when Li migrates into the structure. During materials synthesis, temperature and chemical potentials (μ) provide the driving forces for phase transformations of the precursors and the compositional changes required to form stable products [41].

To explicitly calculate the various thermodynamic potentials, we rely on statistical mechanics principles, which link the bulk thermodynamic properties of a material with its microscopic states (s) and their associated energy levels (ϵ_s) [39]. Within the canonical ensemble, the probability of s is proportional to its energy weighted by the Boltzmann factor $\exp(-\frac{\epsilon_s}{k_B T})$, as stated in Equation 2.3a, in which the partition function Z is a normalization factor. Z is evaluated as the sum over the Boltzmann factors of each s (Equation 2.3b). For convenience, this expression can be written in terms of the inverse thermal energy ($\beta \equiv \frac{1}{k_B T}$).

$$\text{Prob}(s) = \frac{\exp(-\frac{\epsilon_s}{k_B T})}{Z} = \frac{\exp(-\beta \epsilon_s)}{Z} \quad (2.3a)$$

$$Z = \sum_s \exp\left(-\frac{\epsilon_s}{k_B T}\right) = \sum_s \exp(-\beta \epsilon_s) \quad (2.3b)$$

The partition function Z is a critical quantity, as it provides the link between the microscopic states and the ensemble-averaged thermodynamic potentials [39, 40]. Using Equations 2.3a and 2.3b, it can be shown that U is related to the derivative of Z with respect to β (Equation 2.4a). Furthermore, F is proportional to $\ln Z$ (Equation 2.4b). Since Z is often an infinite sum that cannot be analytically evaluated, it can be practically useful to directly relate F and U (Equation 2.4c), which can be derived by substituting Equation 2.4b into 2.4a and integrating over β from a reference value of β_0 .

$$U \equiv \langle \epsilon \rangle = -\frac{1}{Z} \frac{dZ}{d\beta} = -\frac{d \ln Z}{d\beta} \quad (2.4a)$$

$$F = -\frac{\ln Z}{\beta} \quad (2.4b)$$

$$\beta F(\beta) - \beta_0 F(\beta_0) = \int_{\beta_0}^{\beta} U(\beta) d\beta \quad (2.4c)$$

Using this statistical mechanics formalism, we can calculate the thermodynamic potentials from knowledge of the energies of microstates s . The exact form of each s is dependent

on the forms of excitations (i.e. degrees of freedom) present within each material [39]. All materials exhibit vibrational excitations as the atoms vibrate near their ground state equilibrium positions at elevated temperature, forming collective excitations known as phonons. In this context, s represents a phonon vibrational mode, which can be treated quantum mechanically and solved from first principles, as will be described in Chapters 2.3 and 3.2. The Li superionic conductor and cathode phases we study also exhibit configurational disorder within their crystalline lattices, i.e. the atoms can arrange in a variety of distinct orderings on the lattice sites, with each unique configuration constituting a state s . Within TM oxides such as Li battery cathodes, magnetic ordering can arise from the localized d electron states, which gives rise to magnetic degrees of freedom. In the following sections, we describe how the configurational and vibrational degrees of freedom are treated, as we will analyze these forms of excitations. The magnetic disorder and other degrees of freedom are neglected for simplicity, which turns out to be a useful approximation.

2.2 Configurational disorder and cluster expansions

To treat the configurational free energy (F_{config}), other thermodynamic potentials, and short-range order of disordered materials, we require the energies of unique atomic arrangements of the lattice, which constitute the microstates s within the partition function Z (Equation 2.3b). The total energy of all configurations of a finite supercell can in principle be computed from electronic structure methods such as DFT. However, given the vast number of possible configurations on a large supercell, the computational burden required to evaluate all possible configurational energies would be prohibitive. Therefore, the Z cannot be realistically approximated and the thermodynamic potentials must instead be derived from stochastic methods.

Cluster expansion (CE) formalism

A well-established approach towards treating the configurational disorder is the cluster expansion (CE) and Monte Carlo (MC) sampling method [35, 12]. The CE is a lattice model Hamiltonian that can be parameterized to evaluate the energy (or other properties) of any possible configuration of the lattice with negligible computation cost [34, 42]. Once the CE is properly trained, it can be used in MC simulations, which sample from the probability distributions pertaining to a chosen thermodynamic ensemble (canonical, grand canonical, etc.), commonly through the Metropolis-Hasting algorithm [43]. The properties obtained from MC simulations can be averaged and integrated to obtain various other thermodynamic quantities.

The CE formalism was first derived by Sanchez et al., who built upon the cluster variation method (CVM) previously used to calculate the thermodynamic properties, short-range order, and phase diagrams of alloys [34, 44, 45]. The CE represents the energy E_{CE} (or other

property) as a function of the configuration of the lattice ($\vec{\sigma}$), where $\vec{\sigma}$ is a vector of integers encoding the species occupying each site ($\vec{\sigma} = (\sigma_1, \sigma_2, \dots, \sigma_i, \dots, \sigma_N)$) of a supercell of N sites [35]. The CE functional form is composed of a linear combination of cluster functions $\Phi_\alpha(\vec{\sigma})$ that describe the configuration of the possible clusters of sites α (e.g. pairs, triplets, etc.), each contributing an effective cluster interaction (ECI, or J_α) energy, as shown in Equation 2.5a. To construct the basis of cluster functions $\{\Phi_\alpha(\vec{\sigma})\}$, we first define a set of site basis functions that describe the configuration space of each site i $\{\phi_i(\sigma_i)\}$, which can take the form of sinusoidal functions, polynomials, among others [34, 46]. The number of site basis functions must be at least equal to the number of possible species that can occupy the site, such that $\{\phi_i(\sigma_i)\}$ spans the configuration space. The cluster basis functions $\{\Phi_\alpha(\vec{\sigma})\}$ can then be constructed by taking the tensor product of all ϕ_i (i.e. all possible N -fold products between ϕ_i), as shown in Equation 2.5b.

$$E_{\text{CE}}(\vec{\sigma}) = \sum_{\alpha} J_{\alpha} \Phi_{\alpha}(\vec{\sigma}) \quad (2.5a)$$

$$\Phi_{\alpha}(\vec{\sigma}) \equiv \prod_{i=1}^N \phi_i(\sigma_i) \quad (2.5b)$$

Within $\{\phi_i(\sigma_i)\}$, the constant basis function ($\phi_{i,0} = 1$) is always included, which gives the Φ_{α} a cluster-like structure.

A final step is to formulate $E_{\text{CE}}(\vec{\sigma})$ such that it is invariant with respect to the symmetry operations of the disordered crystal structure. To do so, symmetrically invariant cluster correlation functions can be derived by grouping symmetrically equivalent Φ_{α} into orbits β , and within each β averaging over Φ_{α} to form the correlation function $\Theta_{\beta}(\vec{\sigma})$, as shown in Equation 2.6a, where m_{β} is the multiplicity of β . The CE energy can then be expanded in terms of Θ_{β} and the corresponding J_{β} , which are the ECI normalized per cluster (Equation 2.6b). E_{CE} can be more conveniently recast in the form of Equation 2.6c, in which $\vec{\Pi}$ is a vector of correlation functions (Equation 2.6d) and $\vec{J}_{\beta}$ the vector of ECI that have accounted for the multiplicities m_{β} .

$$\Theta_{\beta}(\vec{\sigma}) = \langle \Phi(\vec{\sigma}) \rangle_{\beta} = \frac{1}{m_{\beta}} \sum_{\alpha \in \beta} \Phi_{\alpha}(\vec{\sigma}) \quad (2.6a)$$

$$E_{\text{CE}}(\vec{\sigma}) = \sum_{\beta} m_{\beta} J_{\beta} \Theta_{\beta}(\vec{\sigma}) \quad (2.6b)$$

$$E_{\text{CE}}(\vec{\sigma}) = \vec{\Pi}(\vec{\sigma}) \cdot \vec{J}_{\beta} \quad (2.6c)$$

$$\vec{\Pi}(\vec{\sigma}) = [\Theta_0 \equiv 1, \Theta_{\beta_1}(\vec{\sigma}), \Theta_{\beta_2}(\vec{\sigma}) \dots] \quad (2.6d)$$

CE parameterization

The cluster interactions J_{β} (Equation 2.6b) are not *a priori* known and can be determined through fitting to a dataset of configurations and corresponding total energies [35], which

are usually computed within electronic structure methods such as DFT. Although the CE energy (Equation 2.6b) can in principle be an infinite sum, in practice the orbits β are truncated up to distance cutoffs that are adjustable (e.g. pairs up to 7 Å and triplets up to 5 Å), which is physically justified as the short-range clusters typically have the greatest interaction strength. It is important to note that the number of β grows quickly with the number of possible components that can occupy each site (i.e. the dimensionality of the sublattice), since the number of site basis functions ϕ_i is commensurate to the dimensionality [47, 34]. Early on, in the study of relatively simple disordered materials such as binary alloys, linear regression was used to fit the J_β [48, 35]. However, when developing a CE of materials containing a greater number of components, the number of β and resulting model size tends to increase rapidly. In this scenario, the regression problem can become under-determined, where the number of training samples is less than the number of model parameters (J_β), which arises because generating DFT data is relatively computationally intensive.

There are several strategies for parameterizing high-dimensional CE models. When treating ionic materials, it has become common practice to include an additional electrostatic potential term (E_{Coulomb}) to describe long-range Coulomb interactions, which can reduce the distance cutoffs of β required to achieve reasonable CE model convergence [49]. The electrostatic term is formulated as follows

$$E_{\text{Coulomb}}(\vec{\sigma}) = \frac{E_{\text{Ewald}}(\vec{\sigma})}{\epsilon_c} \quad (2.7)$$

where E_{Ewald} is the bare electrostatic energy of the ions with idealized oxidation states, often computed with the Ewald summation method [50], and ϵ_c is an effective dielectric constant that screens the electrostatic interaction. The ϵ_c becomes an additional coefficient that must be fitted in conjunction with $\vec{J}_\beta$.

When fitting a CE in the under-determined regime, it is essential to harness regularized linear regression techniques to prevent overfitting, of which the plain linear regression method is prone [35]. Within linear regression, J_β are determined by minimizing the mean-squared error of the model predictions (first term on right side of Equation 2.8a). In regularized linear regression, an additional term (R) is added to penalize a form of norm of $\vec{J}_\beta$ coefficients (second term on right side of Equation 2.8a). A common approach is to penalize the ℓ_1 norm of J_β , which is known as the Lasso regularization technique as shown in Equation 2.8b, where λ is the regularization hyperparameter that determines how strongly the ℓ_1 norm of J_β is penalized [51, 52]. Other norms of $\vec{J}_\beta$ can be penalized, for example the ℓ_2 norm (Equation

2.8c), which is done within Ridge regression [53].

$$\vec{J}_\beta^* = \operatorname{argmin}_J \left\| \mathbf{\Pi} \vec{J}_\beta + \frac{E_{\text{Ewald}}(\vec{\sigma})}{\epsilon_c} - \vec{E} \right\|_2^2 + R(\vec{J}_\beta) \quad (2.8a)$$

$$R(\vec{J}_\beta)_{\text{Lasso}} = \lambda \left\| \vec{J}_\beta \right\|_1 = \lambda \sum_{\beta} |J_\beta| \quad (2.8b)$$

$$R(\vec{J}_\beta)_{\text{Ridge}} = \lambda \left\| \vec{J}_\beta \right\|_2 = \lambda \left(\sum_{\beta} |J_\beta|^2 \right)^{1/2} \quad (2.8c)$$

It can be shown that the penalization of the ℓ_1 norm (Equation 2.8b) serves to reduce the number of non-zero J_β and the magnitudes of J_β , which helps prevent overfitting [52]. The use of Lasso promotes a sparse solution vector, which is often the nature of fitted $\vec{J}_\beta$ within the CE, as well as in models within other fields such as signal processing [51, 52, 54]. The penalization of the ℓ_2 norm (Equation 2.8c) instead would only promote reduced magnitudes of J_β [53, 35]. More recently, regularization methods that simultaneously penalize a combination of various ℓ_0 , ℓ_1 , and/or ℓ_2 norms have been developed, which have demonstrated success in parameterizing sparse high-dimensional CE models with reasonable physical accuracy [55, 56, 57].

Monte Carlo (MC) simulations

Once a physically accurate CE has been parameterized, the energy of any arbitrary ordering of the lattice can be trivially evaluated using Equation 2.6c, which requires negligible computational cost. The CE can then be utilized to perform MC simulations on large supercells to stochastically determine the thermodynamic quantities of a disordered crystal structure. The predominantly used MC algorithm is the Metropolis-Hastings algorithm, which has the following steps for a MC simulation within the canonical ensemble at a fixed temperature [43].

1. Starting from an initial configuration $\vec{\sigma}_0$, propose a new configuration $\vec{\sigma}_1$, which can be a swap of species between two sites.
2. The ratio between the probability of states $\vec{\sigma}_0$ and $\vec{\sigma}_1$ (α) is evaluated as

$$\alpha \equiv \frac{\text{Prob}(\vec{\sigma}_1)}{\text{Prob}(\vec{\sigma}_0)} = \frac{\exp(-\frac{\epsilon_1}{k_B T})}{\exp(-\frac{\epsilon_0}{k_B T})} = \exp\left(-\frac{\epsilon_1 - \epsilon_0}{k_B T}\right) \quad (2.9)$$

which can be derived from Equation 2.3a.

3. Determine whether to accept or reject the proposed σ_1 . Randomly draw a number u between $[0, 1]$. If $\alpha \geq u$, then accept σ_1 ; and if not reject. Note that if $\epsilon_1 \leq \epsilon_0$, then the proposal is always accepted.

This process would iteratively continue for M iterations. Since at each iteration, the acceptance/rejection of σ_i is determined from the probabilities dictated by the canonical ensemble, the average internal energy U of a collection of MC samples can be simply evaluated as the average energy of these samples

$$U = \langle \epsilon \rangle = \frac{1}{M} \sum_{i=1}^M \epsilon_i \quad (2.10)$$

It can be shown that given enough iterations, U and other evaluated properties should converge to the canonical ensemble distribution.

The procedure within a grand canonical (GC)-MC simulation would be analogous, in which the proposal in Step 1 would involve changes in composition, and the Boltzmann factors in Step 2 would take the form $\exp(-\beta(\epsilon_i - \mu N_i))$, reflecting the sampling of the grand canonical ensemble. GC-MC simulations then would require scanning of both T and μ variables. Within ionic materials, it is essential for proposals to have compositional changes that satisfy charge neutrality. More details about these charge-neutral GC-MC simulations were recently formulated by Xie et al. [58], which we harness in our studies.

Other forms of thermodynamic potentials can be derived from thermodynamic integration over the averaged quantities obtained from MC simulations. For example, the Helmholtz free energy F can be calculated by integrating U over $\beta \equiv \frac{1}{k_B T}$

$$\beta F(\beta) - \beta_0 F(\beta_0) = \int_{\beta_0}^{\beta} U(\beta) d\beta \quad (2.11)$$

with the proof shown in Equation 2.4c. Furthermore, the entropy (S) can be calculated as

$$S(T) - S(T_0) = \int_{T_0}^T \frac{c_v(T) dT}{T} \quad (2.12a)$$

$$c_v(T) = \frac{\langle \epsilon^2 \rangle(T) - \langle \epsilon \rangle^2(T)}{k_B T^2} \quad (2.12b)$$

where c_v is the heat capacity. Within Equations 2.11 and 2.12, the reference states T_0 (β_0) are typically chosen from the $T \rightarrow 0$ ($\beta \rightarrow \infty$) or $T \rightarrow \infty$ ($\beta \rightarrow 0$) limits, where F and S can be analytically determined. For phases with a known ground state configuration, the $T \rightarrow 0$ limit is useful, as there is no entropy ($S_0 = 0$) and F is equal to the ground state energy ($F_0 = E_{\text{GS}}$). Meanwhile for disordered phases, the opposite limit of $T \rightarrow \infty$ is more useful, as $S_{\infty} = k_B \ln(\sigma)$ and $\beta F_{\infty} = -\frac{\ln(\sigma)}{k_B}$, where σ is the number of possible configurations of the lattice. For an alloy of d components, there are d possible occupations of each site, so S_{∞} can be trivially evaluated as $k_B \ln(d^N) = N k_B \ln(d)$, where N is the number of sites in the supercell. Within ionic materials however, this expression is not always valid as it accounts for configurations with compositions that are not charge neutral. We will discuss a useful procedure for the case of ionic materials in Chapter 6.6.

2.3 Phonons

The theory to obtain the thermodynamic properties of phonons within the harmonic approximation is well-established within solid-state physics [59, 60, 61]. Convenient analytical forms of the thermodynamic potentials can be derived, which are functions of the phonon frequencies. Within the harmonic approximation, the potential energy surface (E_{pot}) is expanded in a second-order Taylor series with respect to the displacements of atoms from their ground state positions

$$E_{\text{pot}} = E_0 + \frac{\partial E_{\text{pot}}}{\partial R_I} \Delta R_I + \frac{\partial^2 E_{\text{pot}}}{\partial R_I \partial R_J} \Delta R_I \Delta R_J + \text{h.o.} \quad (2.13)$$

where E_0 is the ground state energy, ΔR_I (ΔR_J) represent the displacements of atom I (J), and higher order (h.o.) anharmonic terms are neglected. The first derivative of E_{pot} (the forces) in Equation 2.13 evaluated at the ground state configuration is zero, since the energy is minimized. The second derivative of E_{pot} with respect to displacements of the nuclei is the matrix of second order interatomic force constants (IFC) $D(R_{IJ}) = \frac{\partial^2 E}{\partial R_I \partial R_J}$ and its Fourier transform is the dynamical matrix $D(q)$ (Equation 2.14a) [59, 61]. It can be shown that the eigenvalues of $D(q)$ correspond to the square of phonon frequencies corresponding to mode m with wave vector q (ω_{mq}), while the eigenvectors are the corresponding phonon displacement vectors (u_{mq} in Equation 2.14b).

$$D(q) = \sum_{R_{IJ}} e^{-iqR_{IJ}} D(R_{IJ}) \quad (2.14a)$$

$$D(q)u_{mq} = \omega_{mq}^2 u_{mq} \quad (2.14b)$$

We will describe how $D(q)$ and the resulting phonon band structure can be calculated from electronic structure methods in chapter 3.2.

Once ω_{mq} are determined, the thermodynamic potentials can be calculated from analytical functions of ω_{mq} . An important consideration needed to derive these quantities is that each phonon state (labeled by mq) can be treated as a quantum harmonic oscillator with energy levels $\epsilon_{mq,n} = \hbar\omega_{mq}(n + \frac{1}{2})$, where $n \geq 0$. Furthermore, an arbitrary number of phonons can occupy each energy level n , since phonons are boson particles [60]. It can be shown then that the canonical partition function for a single phonon state (z_{mq}) is

$$z_{mq} = \exp\left(-\frac{\hbar\omega_{mq}}{2k_B T}\right) \frac{1}{1 - \exp\left(-\frac{\hbar\omega_{mq}}{k_B T}\right)} \quad (2.15)$$

Since the phonon states are orthogonal and thus independent of each other within the harmonic approximation, the partition function for the system of phonon modes (Z_{ph}) is simply the product over each z_{mq}

$$Z_{\text{ph}} = \prod_{mq} z_{mq} \quad (2.16)$$

and thus $\ln(Z_{\text{ph}})$ is the summation

$$\ln(Z_{\text{ph}}) = \sum_{mq} \ln(z_{mq}) \quad (2.17)$$

The following expressions for the phonon internal energy and free energy (U_{ph} and F_{ph}) can then be derived from the necessary manipulations of Z_{ph} as introduced in Equations 2.4a and 2.4b [59]

$$U_{\text{ph}}(T) = \sum_{mq} \hbar\omega_{mq} \left[\frac{1}{2} + \frac{1}{\exp\left(\frac{\hbar\omega_{mq}}{k_B T}\right) - 1} \right] \quad (2.18)$$

$$F_{\text{ph}}(T) = \sum_{mq} \frac{\hbar\omega_{mq}}{2} + k_B T \sum_{mq} \ln \left[1 - \exp\left(-\frac{\hbar\omega_{mq}}{k_B T}\right) \right] \quad (2.19)$$

There are certain short-comings for this approach of calculating phonon thermodynamic properties. Higher order anharmonic IFCs are required to achieve better accuracy, especially in systems that are known to be strongly anharmonic [62, 63, 64], such as ferroelectrics, Jahn-Teller complexes, and more. Methods to treat anharmonicity include perturbative treatments, fitting of higher-order IFC matrices, and/or stochastic methods, which require much greater computational cost [65, 66, 63]. Furthermore, we have treated the configurational and vibrational degrees of freedom as separate, though they can be strongly coupled in some systems [67]. It has been shown that capturing the coupling of configurational disorder and vibrational modes can significantly improve the prediction of phase diagrams and other thermodynamic properties. The CE can be reformulated to include temperature-dependent interactions that reflect the configurational dependence of vibrational modes [68]. However, these types of models have only been formulated for binary alloys, while we study higher dimensional ionic materials, so adapting these approaches would require significantly greater computational complexity.

Chapter 3

Electronic Structure Theory

To compute the structural and electronic properties of battery materials, we harness *ab initio* electronic structure theory methods, which are mathematical approximations to solve the many-body Schrodinger equation [30]. These approximations are implemented in various computational codes that have enabled precise calculations of the properties of materials, spanning application areas such as energy storage, semiconductors, 2D materials, alloys, and more [69, 70, 71, 31]. From these methods, we can compute the details of atomic structure, electronic band structure, total energy, vibrational spectra, dielectric properties, and more. With recent developments in formalism, algorithms, and high-performance computing, methods such as density-functional theory (DFT) can be performed in high-throughput, enabling the swift screening of novel material candidates and the construction of high-fidelity databases of computed materials properties [31, 33, 32]. The extensive data generated over the years has recently enabled the training of machine learning (ML) models for accelerated molecular dynamics simulations, inverse materials design, and more [36, 38, 37, 72]. In the context of our *ab initio* thermodynamics analysis, these electronic structure methods quantify the properties of the possible microstates within each material, the knowledge of which are used in statistical mechanics methods to evaluate the ensemble-averaged thermodynamic properties. We primarily harness methods based on DFT, so we will describe the DFT formalism and methods that we apply. This is followed by a briefer summary of many-body perturbation theory, which we will also apply for more accurate electronic structure analysis.

3.1 Density-functional theory (DFT)

DFT is one of the major classes of approximations to the many-body Schrodinger equation (SE) for a system of electrons and nuclei. By assuming that the electronic degrees of freedom relax on time scales orders of magnitude faster than the nuclei, we can invoke the Born-Oppenheimer approximation, which allows the SE to be partitioned into an electronic and nuclear portion [73, 74]. The electronic SE for a system of N electrons, neglecting relativistic

effects, can be written

$$\hat{H}\Psi(r_1, r_2 \dots r_N) = \sum_i^N \left(\frac{-\nabla_i^2}{2} + \sum_R V_{\text{ion}}(r_i - R) + \frac{1}{2} \sum_{j \neq i} \frac{1}{|r_i - r_j|} \right) \Psi(r_1, r_2 \dots r_N) = E\Psi(r_1, r_2 \dots r_N) \quad (3.1)$$

where the terms in the Hamiltonian ($\hat{H}$) correspond to the electrons' kinetic energy, Coulomb attraction between electron i and nucleus at R ($V_{\text{ion}}(r_i - R)$), and electron-electron (el-el) electrostatic repulsion (from left to right, in atomic units). Through solving the SE, one can obtain the wave function $\Psi(r_1, r_2 \dots r_N)$, which encodes all possible observable properties, and the energy levels E of the system [74].

Although Equation 3.1 is exact, it is not analytically solvable beyond $N = 1$ electrons, as it is a differential equation of $3N$ variables that becomes intractable. Thus, for realistic atoms, molecules, and solids, significant approximations are required. DFT – specifically the Kohn-Sham (KS) formulation of DFT – is a commonly used approximation, in which the many-body SE (Equation 3.1) is recast as independent one-electron SE's within an effective potential (v_{eff}), each of which are numerically solvable [73]. This is a form of mean-field approximation to the SE, in which the many-body wave function $\Psi(r_1, r_2 \dots r_N)$ is partitioned into independent wave functions for each electron: $\psi_i(r)$. Mean-field approximations span formulations such as the Hartree, Hartree-Fock, and KS-DFT methods, which differ in the way that electron-electron interactions are treated [73].

Hohenberg and Kohn first formulated the DFT framework by proving that within a fixed external potential set by the ionic nuclei (V_{ion}), there is a one-to-one correspondence between the ground state total energy (E) of an interacting electron system and the electron density $\rho(r)$ [75]. Then E can be expressed as

$$E = \int \rho(r) v_{\text{ion}}(r) dr + F[\rho] \quad (3.2)$$

where $F[\rho]$ is a universal functional of the density

$$F[\rho] = E_{\text{KE}} + E_{\text{Hartree}} + E_{\text{xc}} = -\frac{1}{2} \int \sum_i^N \psi_i^*(r) \nabla^2 \psi_i(r) dr + \int \frac{\rho(r)\rho(r')}{2|r - r'|} dr dr' + E_{\text{xc}}[\rho] \quad (3.3)$$

containing terms that describe the kinetic energy (E_{KE}), el-el repulsion (E_{Hartree}), and a final term that contains all electronic exchange and correlation interactions (E_{xc}). $E_{\text{xc}}[\rho]$ is known as the exchange-correlation functional, the exact form of which is unknown, and the development of approximations to $E_{\text{xc}}[\rho]$ is an active area of research. We will describe the various approximations to $E_{\text{xc}}[\rho]$ later in this chapter.

Kohn and Sham then developed a scheme to derive a set one-electron SE's within an effective potential (v_{eff}) that can be solved self-consistently along with other equations to

arrive at the ground state E_0 and ρ (Equations 3.4) [76]. The one-electron SE's (Equation 3.4a) are derived from applying the variational principle to minimize E , through taking the functional derivative of E (Equation 3.2) with respect to changes in $\rho(r)$, subject to the constraint that the number of electrons is conserved ($\int \rho(r)dr = N$). The one-electron SE's (Equation 3.4a) are solved self-consistently with the other Kohn-Sham equations describing $\rho(r)$ and v_{xc} (Equations 3.4c and 3.4d) iteratively until the total energy is minimized.

$$\left\{ -\frac{\nabla^2}{2} + v_{\text{eff}}(r) \right\} \psi_i(r) = \epsilon_i \psi_i(r) \quad (3.4a)$$

$$v_{\text{eff}}(r) = v_{\text{ion}}(r) + e^2 \int \frac{\rho(r')}{|r - r'|} dr' + v_{xc}(r) \quad (3.4b)$$

$$\rho(r) = \sum_i^N \psi_i^*(r) \psi_i(r) \quad (3.4c)$$

$$v_{xc}(r) = \frac{\delta E_{xc}}{\delta \rho(r)} \quad (3.4d)$$

Within this framework, the energy eigenvalues ϵ_i (Equation 3.4a) are simply Lagrange multipliers that enforce the constraint of fixed N , so by construction do not carry physical meaning. Nevertheless, the electronic structure derived from ϵ_i is often a useful starting point to rationalize the electronic structure [73].

Within crystalline solids, it is important to note that $v_{\text{ion}}(r)$ and $v_{\text{eff}}(r)$ are lattice periodic functions (i.e. $v_{\text{eff}}(r) = v_{\text{eff}}(r + R)$, where R is a lattice vector), which means that the wave functions $\psi_i(r)$ must satisfy Bloch's theorem

$$\psi_i(r) = \psi_{nk}(r) = u_{nk}(r) e^{ikr} \quad (3.5)$$

where n is the band index, k a wave vector within the first Brillouin zone, and $u_{nk}(r)$ is a lattice periodic function [60, 73]. $u_{nk}(r)$ can be expanded over plane waves with reciprocal lattice vectors G and their associated Fourier components $u_{nk}(G)$

$$u_{nk}(r) = \sum_G u_{nk}(G) e^{iGr} \quad (3.6)$$

Given this structure of the Bloch wave functions in materials, it becomes more natural to recast and solve the Kohn-Sham equations (Equations 3.4) in reciprocal space and use a plane-wave basis set to represent ψ_{nk} [77], with the basis set size determined by an energy cutoff. In practice, the Kohn-Sham equations are solved only for the valence electrons, while the core electrons are frozen and represented as part of v_{ion} in the form of pseudopotentials. The main forms of modern pseudopotentials are norm-conserving, ultra-soft, and projector augmented wave (PAW) pseudopotentials [78, 79, 80, 81, 82, 83, 84], all of which we have used in our investigations.

Exchange-correlation functionals

Local density approximation (LDA)

Although DFT is in principle exact, the precise form of the exchange-correlation functional ($E_{xc}[\rho]$) is still unknown. As a first approximation, Kohn and Sham developed the local density approximation (LDA) [76], in which $E_{xc}[\rho]$ can be determined from the exchange-correlation energy per electron of a homogeneous gas of density ρ ($\epsilon_{xc}^{unif}(\rho)$), which has been calculated with high accuracy from quantum Monte Carlo methods [85]. The $E_{xc}[\rho]$ of LDA is

$$E_{xc}^{LDA}[\rho] = \int \rho(r) \epsilon_{xc}^{unif}(\rho(r)) dr \quad (3.7)$$

An analogous extension of LDA that is a functional of the spin density (LSDA) was later derived by von Barth and Hedin [86]. For simplicity, we will neglect spin for the remainder of this chapter, though we note that all functionals described are spin-dependent.

Despite the relative simplicity of the LDA scheme, it has proven to be a useful approximation in materials with slowly varying density, such as main group metals and semiconductors. Specifically, the structural properties predicted within LDA are reasonably accurate for these materials, with absolute errors in lattice parameters typically $\leq 0.1 \text{ \AA}$ [87]. However, the pitfalls within LDA are that the lattice parameters of solids are consistently underestimated by $\sim 5\%$, which is due to the tendency of LDA to over-bind the lattice, as it typically over-predicts the magnitude of cohesive energies by $\sim 20\%$. Within atoms, it was noted that the magnitude of the exchange energy (E_x) tends to be underestimated by $\sim 10 - 15\%$, while the magnitude of the correlation energy (E_c) is overestimated by $\sim 100\%$ [88]. Since the magnitude of E_x tends to be much larger than E_c , these errors mostly cancel each other out, but not completely. Furthermore, the band gaps of materials are usually underpredicted by $\sim 40\%$.

One of the main sources of error in the energies predicted from LDA is the self-interaction error (SIE) that is inherent within nearly all DFT approaches [88, 89]. It can be seen that SIE arises from the Hartree el-el repulsion term in Equation 3.3 ($E_{Hartree} = \int \frac{\rho(r)\rho(r')}{2|r-r'|} dr dr'$), in which $E_{Hartree}$ is non-zero even in the limit of a one electron system. Hence, within this Hamiltonian an electron experiences a Coulomb interaction with itself, which is clearly not physical. In principle, the exact E_{xc} would precisely cancel out the SIE, but currently no approximation of E_{xc} can achieve this.

Generalized gradient approximation (GGA)

The LDA can be built upon by including information about the spatial derivative of ρ . The generalized gradient approximation (GGA) achieves this, as it is a functional of ρ and $\nabla\rho$ ($E_{xc}^{GGA} = f(\rho, \nabla\rho)$), the form of which is categorized within "semi-local" density functional approximations [90, 91]. The inclusion of $\nabla\rho$ allows for E_{xc}^{GGA} to be parametrized to satisfy

more types of constraints, norms, and limits of E_{xc} that have been previously derived, leading to improvements in predicted properties compared to LDA. Although the exact functional form of GGA's will not be shown here, they are commonly formulated to enhance E_{xc} relative to the uniform electron gas (LDA), as described by

$$E_{xc}^{GGA} = \int \rho(r) \epsilon_{xc}^{unif}(\rho) F(\rho, \nabla \rho) dr \quad (3.8)$$

where $F(\rho, \nabla \rho)$ is the enhancement factor [90].

The most commonly used form of GGA is the PBE functional derived by Perdew, Burke, and Ernzerhof [90], which has been shown to significantly improve upon the LDA in the prediction of cohesive energies of solids and atomization energies of molecules [92, 93, 87]. Despite this success, PBE tends to predict lattice parameters with errors similar in magnitude to the LDA – though with the key difference being that PBE tends to *overpredict* lattice parameters. Curiously, it has been found that the LDA commonly predicts phonon frequencies with better accuracy than PBE [94, 93]. A more recently parametrized version of GGA that significantly remediates PBE's overestimation of lattice parameters is PBEsol [95], though this comes at the expense of larger errors in cohesive/atomization energies [87]. Neither of these forms of GGA significantly improve the prediction of band gaps compared to the LDA, which indicates that substantial SIE is also present within GGA.

Meta-GGA

The so-called meta-GGA approach builds upon GGA by including also the second derivative of either ρ or the individual orbitals ψ_i in its functional form. An exemplar meta-GGA functional is the strongly constrained and appropriately normed (SCAN) functional, which specifically is a functional of the kinetic energy density ($\tau \equiv \frac{1}{2} \sum_i |\nabla \psi_i|^2$), in addition to $\nabla \rho$ and ρ (i.e. $E_{xc}^{SCAN} = f(\rho, \nabla \rho, \tau)$ [96]). The inclusion of τ enables SCAN to be parametrized to more constraints and norms compared to GGA. This construction helps enable SCAN to provide a faithful description of more diverse types of chemical bonding compared to previously derived functionals [97, 98]. Most notably, SCAN can accurately describe the energy differences and ordering of the various polymorphs of ice, which contain significant long-range van der Waals interactions that other semi-local functionals fail to capture [97]. In general, SCAN outperforms previously proposed meta-GGA, GGA, and LDA approaches, as it can more reliably predict ground state structures, lattice parameters, and formation energies in many classes of materials, including TM oxides exhibiting localized d/f electron states [87, 99, 98, 100]. A key drawback of SCAN is that the computational expense is generally several times greater than PBE and often has convergence issues. More recently, a revised and regularized version of SCAN (r²SCAN) has been developed that mostly alleviates the convergence issues, while generally maintaining the accuracy of SCAN [101, 102]. Given the reasonable reliability and computational cost of r²SCAN, we will often use this functional throughout these studies.

Self-interaction correction schemes

Although SCAN and r²SCAN improve upon the accuracy of other semi-local functionals in many cases, they still fail to reasonably predict certain properties such as band gaps and TM magnetic moments [103, 104]. The prediction of electronic band structure and phase stability is especially worse in materials containing correlated and localized *d* and/or *f* electron states, such as TM oxides. In fact, for several TM monoxides that are known insulators, the LDA and GGA spuriously predict metallic ground states [105, 106]. These pitfalls can primarily be attributed to the SIE and other delocalization errors that are inherently present in all semi-local functionals [88]. Furthermore, it has been shown that the exact E_{xc} should be piecewise linear with respect to electron count and should contain a derivative discontinuity at integer electron counts — features that all forms of semi-local DFT lack [88, 89, 107]. These self-interaction and related delocalization errors can be alleviated through applying approaches such as hybrid functionals and Hubbard corrections, which can lead to improved description of energetics, electronic structure, and other properties within semiconductors and insulators.

Hybrid functionals

In the hybrid functional scheme, the exchange energy (E_x) is computed using a combination of E_x from a semi-local functional and Hartree-Fock (HF) exchange (E_x^{HF}) [108]. The rationale behind this approach is that E_x^{HF} exactly cancels out the SIE of the exchange energy inherent within E_{Hartree} (Equation 3.3) [73, 88]. Thus, mixing a fraction of "exact" HF exchange can improve the prediction of E_x and alleviate SIE. A key problem within hybrid functionals is that the fraction of HF exchange (α) is an adjustable parameter, the ideal value of which is not known *a priori*, and can differ substantially by material. Furthermore, the calculation of E_x^{HF} requires a non-local exchange integral of the form

$$E_x^{\text{HF}} = \frac{1}{2} \int \sum_i \sum_j \frac{\psi_i^*(r_i) \psi_j^*(r_j) \psi_j(r_i) \psi_i(r_j)}{|r_i - r_j|} dr_i dr_j \quad (3.9)$$

which is computationally intensive to evaluate. An approximation to reduce the computational load of E_x^{HF} is to apply a range-separation scheme, which partitions E_x into a short-range (E_x^{SR}) and long-range (E_x^{LR}) component, effectively capturing the screening of electronic exchange. Within the Heyd-Scuseria-Ernzerhof (HSE) range-separated hybrid-GGA approach, a fraction (α) of E_x^{SR} is computed using E_x^{HF} while the remaining fraction ($1 - \alpha$) is computed using PBE [109, 110]. Meanwhile, E_x^{LR} and the correlation energy (E_c) are also evaluated using PBE. The distance cutoff between SR and LR components is determined by another adjustable parameter γ . The breakdown of the HSE exchange-correlation energy (E_{xc}^{HSE}) can be written as follows.

$$E_{xc}^{\text{HSE}} = \alpha E_x^{\text{HF,SR}}(\gamma) + (1 - \alpha) E_x^{\text{PBE,SR}}(\gamma) + E_x^{\text{PBE,LR}} + E_c^{\text{PBE}} \quad (3.10)$$

The key benefit of the range-separation scheme of the HSE hybrid-GGA approach is that the evaluation of E_x^{HF} (Equation 3.9) is truncated to shorter distances, dramatically speeding up the computation [109]. However, even with this improved computational efficiency, HSE is usually an order of magnitude more computationally intensive than PBE.

Previously conducted benchmarks have shown that the HSE hybrid-GGA method significantly improves upon GGA and LDA in the prediction of lattice parameters, band gaps, magnetic properties, and oxidation energies in various materials [110, 111, 112]. The improvements realized by hybrid-GGA methods can be attributed to the reduced SIE by incorporating a fraction of HF exchange, which in turn reduces the delocalization errors within semi-local DFT.

A fundamental challenge within the HSE method and other range-separated hybrid functionals is the selection of adjustable parameters α and γ , which determine the amount of HF exchange and how strongly these interactions are screened within the lattice. A commonly used version of HSE is the HSE06 functional, which fixes the α and γ parameters to be 0.25 and 0.11 Bohr⁻¹, which works well in many systems and thus we harness it in our studies [113]. More physically driven and self-consistent approaches towards determining α and other screening parameters involve *ab initio* calculations of dielectric tensors [114] and satisfying Koopman’s ionization potential theorem, a condition that restores the derivative discontinuity to E_{xc} [115, 116, 117]. These approaches have been shown to yield more precise electronic structure and magnetic properties compared to HSE, though at the expense of even greater computational cost.

Hubbard-corrected DFT

Another commonly used approach to reducing SIE in correlated materials is the application of Hubbard model corrections to a semi-local functional. The Hubbard model, first formulated actually before the advent of DFT, is a relatively simple Hamiltonian that can describe the electronic structure of strongly correlated electron systems, in which the on-site Coulomb repulsion between localized d or f states (often termed U) is much larger than the hybridizing interactions (V) with orbitals on neighboring sites [118]. Notably, the Hubbard model can predict the existence of a band gap within Mott insulators containing partially filled d states, whereas conventional band theory would predict a metallic state. The band gaps of Mott insulators largely arise from the relatively strong U interaction in correlated manifolds. However, the Hubbard model Hamiltonian is not analytically solvable for real materials, thus requiring sophisticated many-body approaches such as dynamical mean-field theory (DMFT) to approximate the solutions [119, 120].

Nevertheless, the success of the Hubbard model in at least qualitatively describing the physics of correlated electrons motivated the addition of a Hubbard U energy term to the semi-local DFT Hamiltonian to improve the treatment of correlated materials [105]. Specifically, the Hubbard U corrections are typically applied only on the localized d/f orbital

manifolds (which we will refer to as Hubbard manifolds), while the remaining states are treated within semi-local DFT – a scheme known as the DFT+ U method. The DFT+ U total energy can be formulated as

$$E_{\text{DFT}+U} = E_{\text{DFT}} + \sum_I \frac{U_I}{2} \text{Tr}[\mathbf{n}^I(1 - \mathbf{n}^I)] \quad (3.11)$$

in which E_{DFT} is the total energy from the semi-local functional, I is the index of TM sites, U_I is an adjustable parameter quantifying the Hubbard energy penalty, Tr is the trace, and $\mathbf{n}^I$ are the occupation matrices of the Hubbard manifolds [121, 106, 122]. Specifically, $\mathbf{n}^I$ is a projection onto atomic-like orbitals corresponding to the correlated TM orbitals ($|\phi_{m,I}\rangle$) centered on site I

$$\mathbf{n}^I = \sum_m |\phi_{m,I}\rangle \langle \phi_{m,I}| \quad (3.12)$$

the trace of which yields the occupation number of the Hubbard manifold. The Hubbard U energy (second term on the right side of Equation 3.11) effectively introduces an energy penalty for fractional occupation of the Hubbard manifold, since this contribution would be zero if the state is either fully occupied or unoccupied [122]. Thus, the Hubbard U correction helps enforce electron localization onto these orbitals. Importantly, the inclusion of Hubbard U only marginally increases the computation cost compared to the parent semi-local functional.

Early on, the Hubbard U correction was augmented to LDA in the so-called LDA+ U approach, which successfully predicted insulating ground states in various TM monoxide insulators (e.g. CuO, CoO, FeO), whereas plain LDA predicted spurious metallic ground states [121, 106]. Later on, Hubbard U corrections were also added to GGA functionals, which also considerably improved predictions of the electronic structure, oxidation reaction enthalpies, and magnetic properties compared to GGA [123]. More recently, it has been shown that Hubbard U corrections added to $r^2\text{SCAN}$ can also improve the predicted oxidation enthalpies and magnetic properties, though $r^2\text{SCAN}$ tends to not predict spurious metallic states in insulating TM oxides [103, 104]. The required U corrections for $r^2\text{SCAN}$ tend to be much smaller than in GGA, which reflects the lower degree of SIE within $r^2\text{SCAN}$ compared to GGA [104]. Besides purely on-site U contributions, it has been shown that applying an additional inter-site Hubbard V parameter (GGA + U + V) – e.g. a hybridizing interaction between TM- $3d$ and nearest O- $2p$ states – can further improve predictions of structural, energetic, and magnetic properties in TM oxides exhibiting strong TM-O covalency [124, 125, 126, 124, 127]. The total energy within DFT + U + V is

$$E_{\text{DFT}+U+V} = E_{\text{DFT}} + \sum_I \frac{U_I}{2} \text{Tr}[\mathbf{n}^I(1 - \mathbf{n}^I)] - \sum_{I,J} \frac{V_{IJ}}{2} \text{Tr}[\mathbf{n}^{IJ} \mathbf{n}^{JI}] \quad (3.13)$$

The Hubbard parameters (HP) are generally determined either by empirical fitting of experimentally known properties (e.g. band gaps, oxidation enthalpies) [123, 103, 104], or

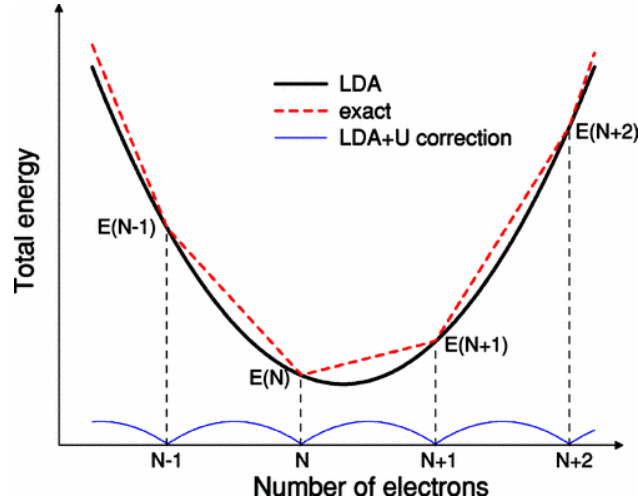


Figure 3.1: Schematic of the LDA, exact DFT, and LDA+ U correction energy as a function of electron count. Reproduced from Cococcioni et al [122].

from *ab initio* calculations, which can be based on linear response DFT [122, 128, 129, 130], constrained random-phase approximation [131, 132, 133], Hartree-Fock based methodologies [134, 135, 136, 137] and machine learning techniques [138, 139, 140]. When HP are obtained from empirical fitting, they are generally held constant for each TM element across all the considered structures. This scheme is frequently used, especially for high throughput workflows, as the computationally expensive calculation of HP can be avoided [123, 71, 31]. However, the *ab initio* calculated HP for a given species can vary significantly depending on the local environment and oxidation state [124, 127] – variations that cannot be captured by empirical fitting procedures. Importantly, it was shown by Cococcioni et al. that the linear response DFT method yields self-consistent HP that can precisely correct for the SIE of the Hubbard manifolds within semi-local functionals [122]. Specifically, the computed Hubbard energy contributions directly correspond to the curvature (second derivative) of the energy with respect to changes in Hubbard orbital occupations, as shown in the schematic of Figure 3.1. The curvature of the DFT (LDA) total energy observed in Figure 3.1 is a spurious feature of semi-local DFT that stems from the SIE. By correcting this spurious energy curvature, piecewise linearity and the derivative discontinuity can be restored to E_{xc} , which are features of a hypothetically exact E_{xc} .

3.2 Linear response DFT and DFPT

As discussed in the previous section, linear response (LR)-DFT can be used to self-consistently calculate HPs within the DFT+ U (+ V) method [122, 125, 128], which we harness in our studies. More broadly, LR-DFT is an important framework that enables the calculation of a wide

range of materials properties, spanning phonon dispersions, dielectric tensors, Born effective charges, chemical shielding tensors, and more [61, 141, 142, 143]. Generally, within LR-DFT a perturbation to a DFT-derived ground state is introduced, which induces changes to the electronic structure that can be used to derive the various response functions of the material.

In certain forms of LR-DFT, a central quantity to determine is the second derivative of the energy with respect to a perturbation of v_{eff} (Equation 3.4b) [61]. Within the harmonic phonon approximation, the second derivative tensor of the total energy with respect to displacements of the nuclei ($D(R_{IJ}) \equiv \frac{\partial^2 E}{\partial R_I \partial R_J}$) and its Fourier transform $D(q)$ (the dynamical matrix) are needed to calculate the phonon frequencies, as discussed in Chapter 2.3 [59]. Meanwhile, to calculate self-consistent HPs within DFT+ U (+ V), the essential quantity is the second derivative of the energy with respect to changes in Hubbard orbital occupations ($\chi_{IJ} \equiv \frac{\partial^2 E}{\partial f_I \partial f_J}$) in a constrained DFT calculation [122, 129]. In the cases of phonon and HP calculations, the second order response matrices $D(R_{IJ})$ and χ_{IJ} , respectively, can be calculated in real space by directly applying the relevant perturbations of the ground state on a supercell, and evaluating the second derivative of the energy using finite differences [129, 59]. Within this finite differences approach, relatively large supercells must be used with lattice parameters commensurate to the long-wavelength perturbations, which can lead to relatively high computation cost.

These LR-DFT schemes can be equivalently recast within the density-functional perturbation theory (DFPT) approach, which can calculate the second-order response matrices from evaluating first-order changes to the DFT ground state orbitals $\psi_{nk}(r)$ and band structure ϵ_{nk} . DFPT is generally formulated in reciprocal space, allowing for the phonon band structure (and other properties) to be solved on the primitive structure as opposed to supercells, which can be much more computationally efficient [61]. To formulate DFPT, it can be shown that the second derivative of the energy with respect to an arbitrary perturbation λ_n is dependent on the first derivative of the electron density (ρ) with respect to λ_n . For example, it can be written for the phonon problem [61]

$$\frac{\partial^2 E}{\partial \lambda_I \partial \lambda_J} = \int \frac{\partial \rho(r)}{\partial \lambda_I} \frac{\partial v_{\text{ion}}}{\partial \lambda_J} dr + \int \frac{\partial^2 v_{\text{ion}}(r)}{\partial \lambda_I \partial \lambda_J} \rho(r) dr \quad (3.14)$$

where v_{ion} is the interaction between electrons and nuclei. The first derivative of $\rho(r)$ can be approximated by applying first-order perturbation theory on the DFT ground state wavefunctions $\psi_{nk}(r)$, as described by the Sternheimer equation (Equation 3.15a) [61]. This equation, in conjunction with linearized versions of other Kohn-Sham equations (Equations 3.15b - 3.15d), form a set of equations that are solved self-consistently to obtain $\Delta\rho(r)$ and

in turn the response matrices.

$$\{H_{\text{DFT}} - \epsilon_{nk}\} \Delta\psi_{nk}(r) = -\{\Delta v_{\text{eff}} - \Delta\epsilon_{nk}\} \psi_{nk}(r) \quad (3.15a)$$

$$\Delta\rho(r) = 4\text{Re} \sum_{nk} \psi_{nk}^*(r) \Delta\psi_{nk}(r) \quad (3.15b)$$

$$\Delta v_{\text{eff}}(r) = \Delta v_{\text{ion}} + \int \frac{\Delta\rho(r')}{|r - r'|} dr' + \frac{\partial v_{\text{xc}}}{\partial \rho} \Delta\rho \quad (3.15c)$$

$$\Delta\epsilon_{nk} = \langle \psi_{nk} | \Delta v_{\text{eff}} | \psi_{nk} \rangle \quad (3.15d)$$

These equations can be recast in reciprocal space, and it can be shown that the linear response to each wave vector (q) component of the perturbation are decoupled from each other. Thus, the response matrices of the phonon and HP problems can be evaluated at arbitrary wave vector q , enabling the calculation of properties such as phonon frequencies across the Brillouin zone and self-consistent Hubbard parameters using the primitive cell.

3.3 GW

As discussed in Chapter 3.1, one of the major shortcomings of all semi-local DFT functionals is the relatively poor description of electronic band structures, and in particular the band gap. A more rigorous *ab initio* framework to evaluate the band structure is the GW approximation, as pioneered by Hybertsen and Louie [144]. GW is a many-body perturbation theory (MBPT) approach of capturing the el-el interactions, and treats the electrons (and holes) as quasiparticles – as opposed to independent electrons in the DFT formalism [73]. It has been shown that GW usually predicts quasiparticle band structures and energy gaps with far superior accuracy compared to semi-local DFT for a range of semiconductors and insulators [144, 115]. The improved results reflect the more rigorous treatment of many-electron interactions within GW , though it comes at much higher computational cost compared to DFT.

In GW , the electronic correlation and exchange are approximated within the self-energy operator (Σ) as the first term in the perturbative expansion of the screened Coulomb interaction (W) [144, 145]

$$\Sigma = iGW \quad (3.16)$$

where G is the Green's function. The GW Hamiltonian and eigenvalue problem is stated as [144]

$$\left\{ -\frac{\nabla^2}{2} + v_{\text{ion}}(r) + v_{\text{Hartree}} \right\} \psi_{nk}(r) + \int \Sigma(r, r', \epsilon_{nk}) \psi_{nk}(r') dr' = \epsilon_{nk} \psi_{nk}(r) \quad (3.17)$$

The form of this equation is nearly identical to the DFT one-electron SE (Equations 3.4a and 3.4b), with the only difference being that the integral of Σ in Equation 3.17 replaces $v_{\text{xc}}(r)$

in Equation 3.4b. Σ is a non-local operator that captures the screened electronic Coulomb interactions at any length scale, whereas semi-local DFT approximates only the short-range electronic interactions.

To evaluate Σ (Equation 3.16), the G and W terms are constructed from a set of orbitals and energies, which are usually obtained from DFT in the first iteration. The essential ingredient needed to construct the Coulomb interaction W is the dielectric tensor $\epsilon(q, \omega)$, which can be calculated from the random-phase approximation (RPA). It was shown early on that including the wave vector (q) and frequency (ω) dependence within $\epsilon(q, \omega)$ are essential for greater accuracy [144]. When G and W are constructed from DFT orbitals and energies, the calculated quasiparticle orbitals $\psi_{nk}(r)$ and energies ϵ_{nk} constitute a renormalization of the DFT orbitals and band energies, arising from the more detailed treatment of screened electron-electron interactions within GW . While GW generally performs well for predicting the band gaps of conventional semiconductors and insulators, a careful selection of the DFT starting point has to be made when dealing with correlated TM oxides, as the accuracy can heavily depend on the quality of the electronic ground state, especially for one-shot calculations [115, 146].

Chapter 4

Phase Stability of Li-P-S Superionic Conductors

4.1 Introduction

The pseudo-binary $\text{Li}_2\text{S-P}_2\text{S}_5$ composition space has proven to be a particularly rich source of promising Li superionic conductors for next-generation solid-state batteries [10]. Several crystalline compounds can be synthesized by combining Li_2S and P_2S_5 precursors in varying ratios (Figure 4.1a)[10], with the notable phases being the α , β , and γ polymorphs of Li_3PS_4 , high-temperature (HT) and low-temperature (LT)- Li_7PS_6 , and $\text{Li}_7\text{P}_3\text{S}_{11}$. Among these, α - Li_3PS_4 , β - Li_3PS_4 , HT- Li_7PS_6 , and $\text{Li}_7\text{P}_3\text{S}_{11}$ are superionic conductors [147, 148]. Although amorphous phases with these compositions also exist[149, 150, 151], the focus of our study will be on understanding the relative phase stability of the crystalline phases only.

The crystalline phases in the $\text{Li}_2\text{S-P}_2\text{S}_5$ space are composed of periodically arranged PS_4 tetrahedra, which are either isolated or form P_2S_7 ditetrahedra. Li atoms are located in between these units and coordinated by S atoms. The Li_7PS_6 polymorphs also contain free S atoms that are only coordinated with Li atoms. Different phases can be identified by their distinct orientation of PS_4 and P_2S_7 groups. The Li_3PS_4 and Li_7PS_6 polymorphs are all composed of isolated PS_4 groups. In γ - Li_3PS_4 , these PS_4 groups are uni-directional, with all apexes facing the same direction (apexes face out of the page in Figure 4.1b). In β - Li_3PS_4 , PS_4 groups are arranged in alternating zig-zag chains, with each chain containing apexes that face the same direction, while apexes in the adjacent chain face the opposite direction (Figure 4.1c) [152]. The α - Li_3PS_4 polymorph also contains PS_4 with oppositely facing apexes, but these are arranged in alternating columns (Figure 4.1d). In both Li_7PS_6 polymorphs, all PS_4 groups face the same direction, but differ in their spatial distributions [153]. In LT- Li_7PS_6 , PS_4 are arranged with orthorhombic symmetry (Figure 4.1e), while in HT- Li_7PS_6 the PS_4 are arranged with face centered cubic (FCC) symmetry (Figure 4.1f) [153]. $\text{Li}_7\text{P}_3\text{S}_{11}$ is composed of both P_2S_7 and PS_4 units (Figure 4.1g)[154].

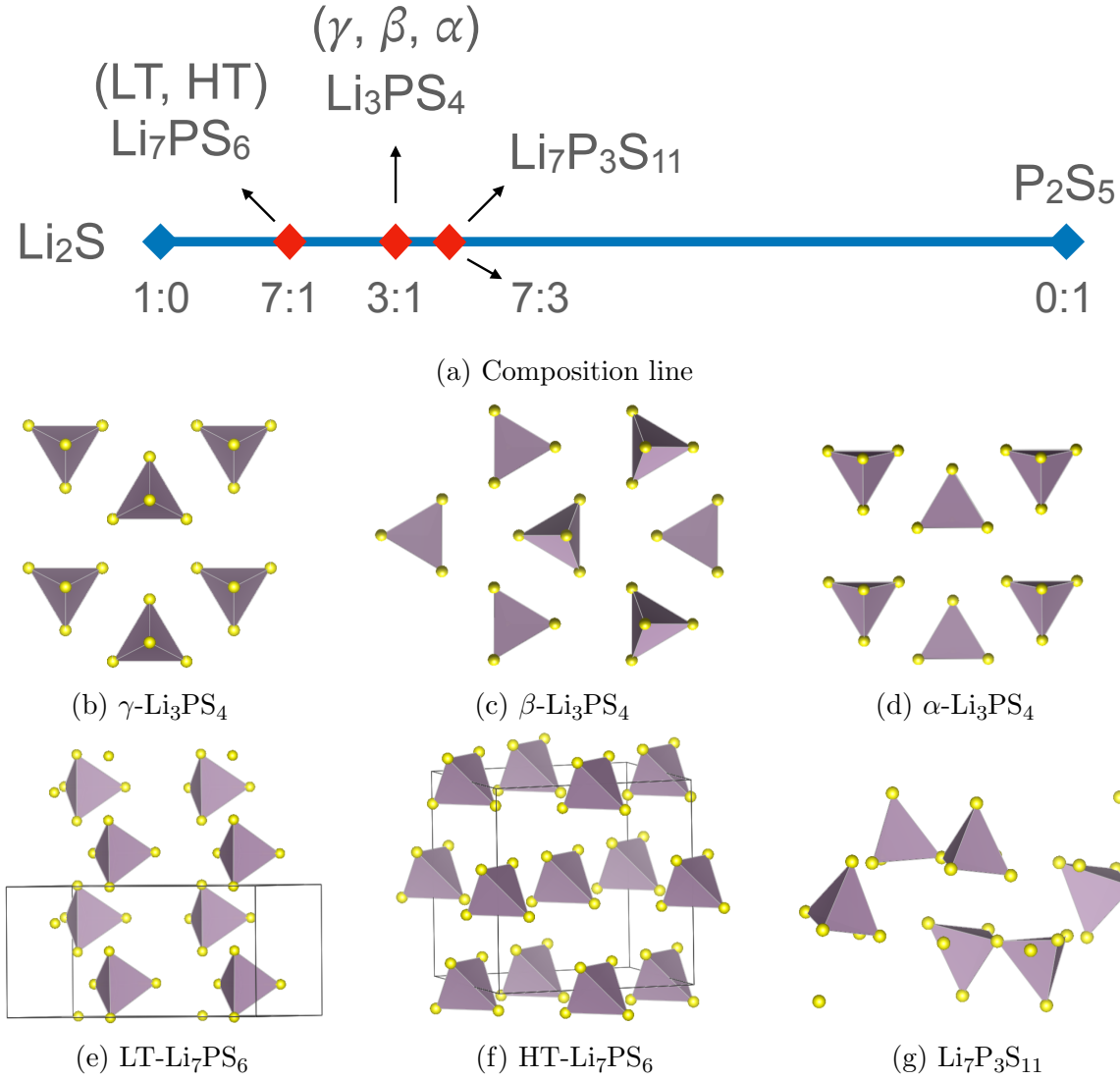


Figure 4.1: Composition line and arrangements of PS_4 tetrahedral units in the Li_2S - P_2S_5 system. a) Location of Li_7PS_6 , Li_3PS_4 , and $\text{Li}_7\text{P}_3\text{S}_{11}$ on the composition line, labeled by the ratios of Li_2S to P_2S_5 . Arrangements of PS_4 and P_2S_7 units in b) γ - Li_3PS_4 , c) β - Li_3PS_4 , d) α - Li_3PS_4 , e) LT- Li_7PS_6 , f) HT- Li_7PS_6 , g) $\text{Li}_7\text{P}_3\text{S}_{11}$. Unit cell boxes are drawn for LT- Li_7PS_6 and HT- Li_7PS_6 to show their cubic and orthorhombic PS_4 arrangement, respectively.

According to previous experimental and computational studies, the superionic conductor phases are all metastable at ambient temperature [10, 151]. Among the Li_3PS_4 polymorphs, γ is the stable phase at room temperature but has low Li conductivity, while β and α are the high temperature fast-conducting phases [152, 155]. β - Li_3PS_4 has been stabilized at room temperature as nanoporous particles from solution-state synthesis [156, 157]. This

phase has also been stabilized through mechanochemical synthesis involving ball milling to form an amorphous phase, and a subsequent heat treatment to recrystallize [150]. An analogous Si-doped $\text{Li}_{3.25}\text{Si}_{0.25}\text{P}_{3.75}\text{S}_4$ structure, where Si substitutes into phosphorus (P) sites, has also been stabilized at room temperature [158]. $\alpha\text{-Li}_3\text{PS}_4$ has recently also been stabilized at room temperature via a rapid heating and quenching technique [159]. This discovery indicates that the energy differences between the three Li_3PS_4 polymorphs at room temperature should be small, allowing for the metastable α and β to be thermodynamically accessible at ambient temperature. $\text{HT-Li}_7\text{PS}_6$ is only stable at elevated temperatures ($T > 483$ K) [153], but has been successfully stabilized at room temperature through halide atom substitution into S sites, typically to form the $\text{Li}_6\text{PS}_5\text{X}$ composition ($\text{X} = \text{Cl}, \text{Br}, \text{or I}$) [160, 161, 162, 163]. Synthesis of $\text{Li}_7\text{P}_3\text{S}_{11}$ usually requires ball-milling to its amorphous form before recrystallization above its glass transition temperature of around 500 K [164, 154, 10]. Heat treatment at higher temperatures ($T > 800$ K) is not possible, as $\text{Li}_7\text{P}_3\text{S}_{11}$ phase-separates to $\text{Li}_4\text{P}_2\text{S}_6$ and Li_3PS_4 [164].

The metastable nature of these superionic conductors motivates our first-principles study with the objective to understand their thermodynamic accessibility at finite temperature, rationalize experimental trends, and potentially propose new synthesis procedures. To model the free energy of each phase, we consider contributions from the electronic structure, configurational disorder, and vibrational modes. We find that including both configurational and vibrational entropy is necessary to correctly predict free energies, in agreement with a previous study on the $\text{Li}_{1+2x}\text{Zn}_{1+x}\text{PS}_4$ system [165].

We model configurational Li-vacancy disorder using the cluster expansion (CE) and Monte Carlo (MC) simulation approach [34, 35, 48, 12]. To properly model the configurational disorder in $\text{HT-Li}_7\text{PS}_6$, $\alpha\text{-Li}_3\text{PS}_4$, $\beta\text{-Li}_3\text{PS}_4$, and $\text{Li}_7\text{P}_3\text{S}_{11}$, we require accurate structural models to define the set of distinct sites that Li can occupy, which we refer to as the Li sublattice. There are conflicting reports about the specific sites that make up the Li sublattices arising from different characterization techniques. More specifically, in $\alpha\text{-Li}_3\text{PS}_4$, $\beta\text{-Li}_3\text{PS}_4$, and $\text{HT-Li}_7\text{PS}_6$, neutron diffraction (ND) refinements [155, 160] have identified more Li sites and increased site disorder as compared to X-ray diffraction (XRD) refinements [152, 166, 153]. In $\text{Li}_7\text{P}_3\text{S}_{11}$, XRD and ND identify fully ordered, but entirely different Li sublattices [154, 167]. A more recent ab-initio molecular dynamics (AIMD) study proposing 15 potential Li sites in $\text{Li}_7\text{P}_3\text{S}_{11}$ introduces uncertainty to the exact state of Li order, since these new sites can in principle be partially occupied [168]. Because of these conflicting reports, we dedicate a large portion of this study towards clarifying the Li arrangement in these structures, the details of which we find to be essential for recovering experimental thermodynamic trends.

For each disordered phase, we assess the validity of various proposed Li sublattices, primarily by analyzing atomic relaxation distances and comparing Li site disordering behavior to experimental reports. Upon obtaining the most representative Li sublattice, we train

a CE and use it to perform MC sampling to determine the configurational entropy, free energy, and Li site disordering behavior as a function of temperature. Vibrational free energy contributions are captured in the ground state of each phase, by performing harmonic phonon calculations [59]. By incorporating the electronic, vibrational, and configurational free energy contributions, we assess thermodynamic stability in the $\text{Li}_2\text{S-P}_2\text{S}_5$ phase space, recovering well-established experimental observations.

The rest of this chapter is organized as follows. 1) The pseudo-binary $\text{Li}_2\text{S-P}_2\text{S}_5$ phase diagram is presented. The thermodynamic stability of each phase at finite temperature is evaluated and potential synthesis procedures for metastable phases are proposed. 2) For each composition, we discuss the appropriate choice of refined structure for each polymorph by comparing the validity of previously proposed models. Phase stability trends between polymorphs are examined in detail, with a focus on identifying phase transitions and quantifying the contributions of vibrational and configurational entropy towards stability. 3) In the discussion, we draw further connections to previously proposed experimental synthesis strategies, and explore a potential correlation between superionic conductivity and high configurational entropy.

4.2 Phase stability in the $\text{Li}_2\text{S-P}_2\text{S}_5$ system

The pseudo-binary $\text{Li}_2\text{S-P}_2\text{S}_5$ phase diagram is presented in Figure 4.2a and the energies above the hull (E_{hull}) as a function of temperature are shown in Figure 4.2b. The convex hull is a typical construction to obtain stable phases and represents the collection of thermodynamic ground states into which all other phases have a driving force to convert [169]. At 0 K, the only stable phases on the convex hull are $\gamma\text{-Li}_3\text{PS}_4$ and the endpoints, Li_2S and P_2S_5 (Figure 4.2a). At 700 K, HT- Li_7PS_6 is stabilized and appears on the hull. Since reported synthesis procedures for LT and HT- Li_7PS_6 typically do not require mechanical milling or quenching [153, 161], it may be surprising that they are unstable at 300 K—13 and 12 meV/atom above the hull respectively (Figure 4.2b). It is likely that the thermodynamically favored phase separation of HT- Li_7PS_6 to Li_2S and Li_3PS_4 is kinetically hindered at room temperature. Instead, HT- Li_7PS_6 is found to transform to LT- Li_7PS_6 upon cooling, a potentially more facile process as it merely involves shifting the PS_4 locations (Figure 4.1). Thus, an appropriate solid-state synthesis procedure would be to perform sufficiently high temperature ($T > 600$ K) synthesis to stabilize HT- Li_7PS_6 , before a relatively rapid cooling process to bypass the phase separation to Li_2S and Li_3PS_4 .

For the Li_3PS_4 composition, our calculations in Figure 4.2b predict phase transformations from $\gamma \rightarrow \beta \rightarrow \alpha$ with increasing temperature, which is consistent with experiments. Since $\beta\text{-Li}_3\text{PS}_4$ is less than 1 meV/atom above the hull at 300 K (Figure 4.2b), it is plausible that nanoporous synthesis and mechanical milling techniques can lead to its stabilization at room temperature [156, 150]. The $\alpha\text{-Li}_3\text{PS}_4$ polymorph is only slightly less stable than β at 300 K ($E_{\text{hull}} = 4$ meV/atom), which explains why α can also be stabilized at ambient temperature

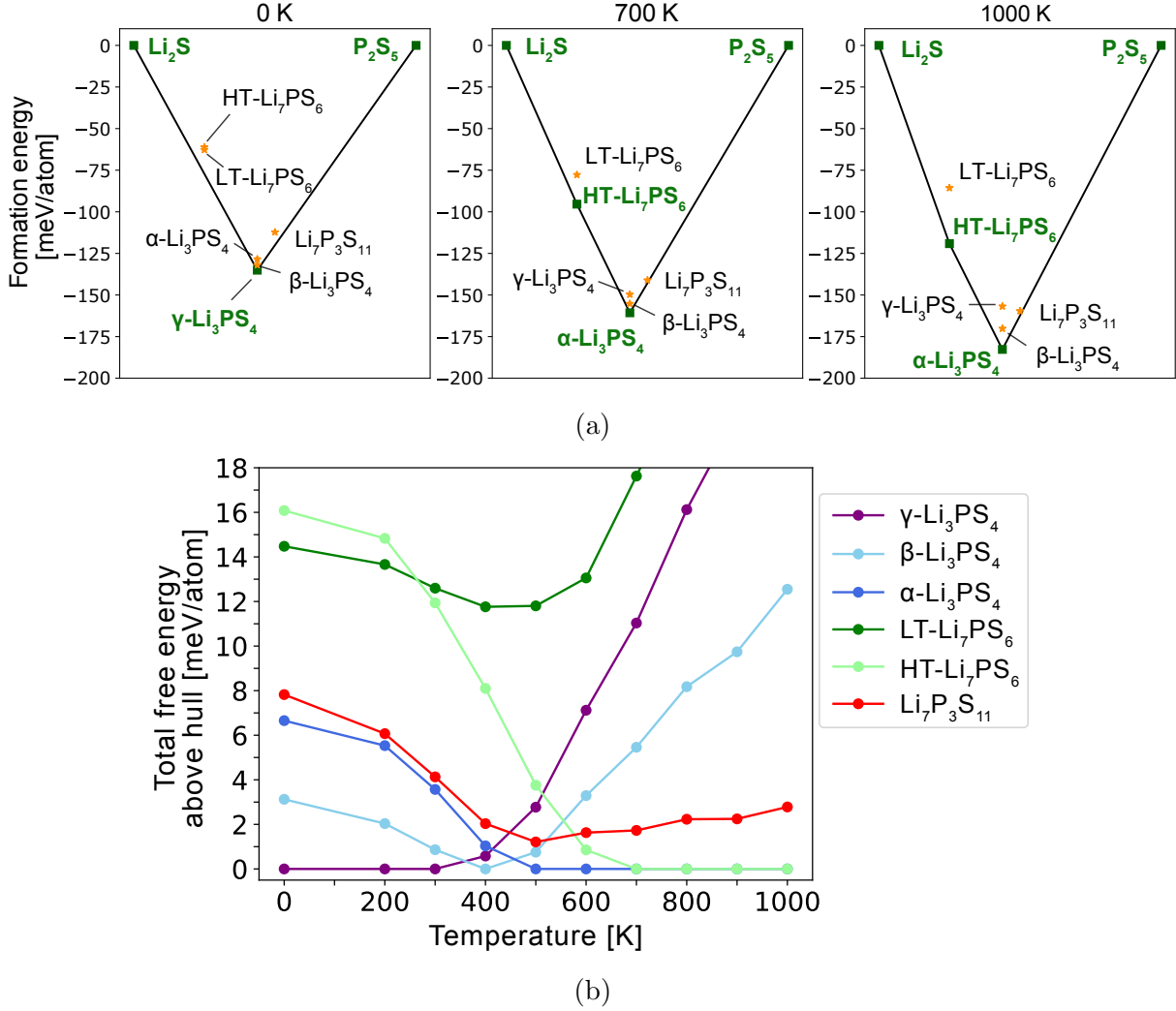


Figure 4.2: Phase stability of the Li_2S - P_2S_5 pseudo-binary system. a) Phase diagram at 0 K, 700 K, and 1000 K. Solid lines denote the convex hull. Stable phases that are on the convex hull are marked with squares and labeled in green. Unstable phases are marked with gold stars and labeled in black. b) Free energy above hull for all phases from 0 to 1000 K.

through a rapid heating and quenching procedure [159]. Rapid heating of the Li_3PS_4 glass to temperatures in the stability range of β enables nucleation of metastable α particles that are only slightly less stable than β , which is possible by the Ostwald step rule [159, 170]. Rapid quenching can then obstruct the commonly observed direct transition from α to γ [152, 155], which is possible as their energy difference is only 4 meV/atom at 300 K.

$\text{Li}_7\text{P}_3\text{S}_{11}$ (red curve in Figure 4.2b) is metastable across all temperatures as its energy is never low enough to be on the convex hull, which agrees with prior experimental studies [164,

154]. At 300 K, it is 4 meV/atom above the convex hull. As temperature increases to 500 K, its E_{hull} decreases to a minimum of 1.4 meV/atom. Further increases in temperature lead to greater E_{hull} . Thus, an ideal synthesis temperature should be around 500 K, corresponding to the minimum E_{hull} . This temperature is remarkably close to its experimentally observed glass transition temperature and helps rationalize why heat treatments near this temperature have been successful for recrystallization [164, 148]. The increasing instability with respect to temperature helps explain the experimentally observed tendency to phase separate to Li_3PS_4 and $\text{Li}_4\text{P}_2\text{S}_6$ at temperatures greater than 800 K [150]. The source of this instability is the competition with $\alpha\text{-Li}_3\text{PS}_4$, its neighboring stable point, which lowers its free energy more with increasing temperature, therefore increasing the convex hull depth (Figure 4.2a). We will show in the next section that this arises from the high configurational entropy in $\alpha\text{-Li}_3\text{PS}_4$.

4.3 Li_3PS_4 polymorphs

$\gamma\text{-Li}_3\text{PS}_4$ ($\text{Pnm}2_1$) is the stable polymorph at room temperature and has a very low Li conductivity of $3(10^{-4})$ mS/cm [152]. The reported XRD and ND refinements are in excellent agreement with each other, showing an ordered Li sublattice comprising of fully occupied Li1 (4b) and Li2 (2a) sites. Since there is no ambiguity in these refinements, we use this structure to model $\gamma\text{-Li}_3\text{PS}_4$ [152, 155].

$\beta\text{-Li}_3\text{PS}_4$ structure

Upon heating, γ transforms to $\beta\text{-Li}_3\text{PS}_4$ at around 575 K, crystallizing in the orthorhombic Pnma space group, which leads to a lattice volume expansion by $\sim 3\%$ [152]. The zig-zag ordering of PS_4 units generates a different Li sublattice with more sites than in γ , leading to the potential for disorder. At around 600 K, XRD refinements have reported Li atoms occupying Li1' (8d), Li2' (4b), and Li3' (4c) sites, with fractional occupancies of 1, 0.7, and 0.3, respectively (XRD refined sites are labeled with apostrophes and ND refined sites without apostrophes for clarity in this discussion)[152]. A more recent ND refinement proposes a slightly different model, with reported site splitting of Li1' (8d) to Li1A (8d) and Li1B (8d), and splitting of Li2' (4b) to Li2 (8d), while retaining its Pnma symmetry [155]. The 4 distinct Li sites refined by ND are all partially occupied.

We analyze the geometric discrepancy between XRD and ND refinements of $\beta\text{-Li}_3\text{PS}_4$ by inspecting the Li coordination environments in the XRD and ND sites. In Figure 4.3a, we show (i) the unit cell, (ii) splitting of Li1' (8d), and (iii) splitting of Li2' (4b). The splitting of the Li1' (8d) site (grey in Figure 4.3a(ii)) in fact yields two distinct sites: Li1A (8d) and Li1B (8d) (green and brown in Figure 4.3a(ii), respectively). Li1A (8d) is essentially identical to Li1' (8d), while Li1B (8d) is its face-sharing neighbor 1.7 Å away. The emergence of Li1B as a new Li site can be detected by ND, while in XRD it has not been detected, likely due to the small X-ray scattering factor of Li. Since Li1A and Li1B sites are not related to each

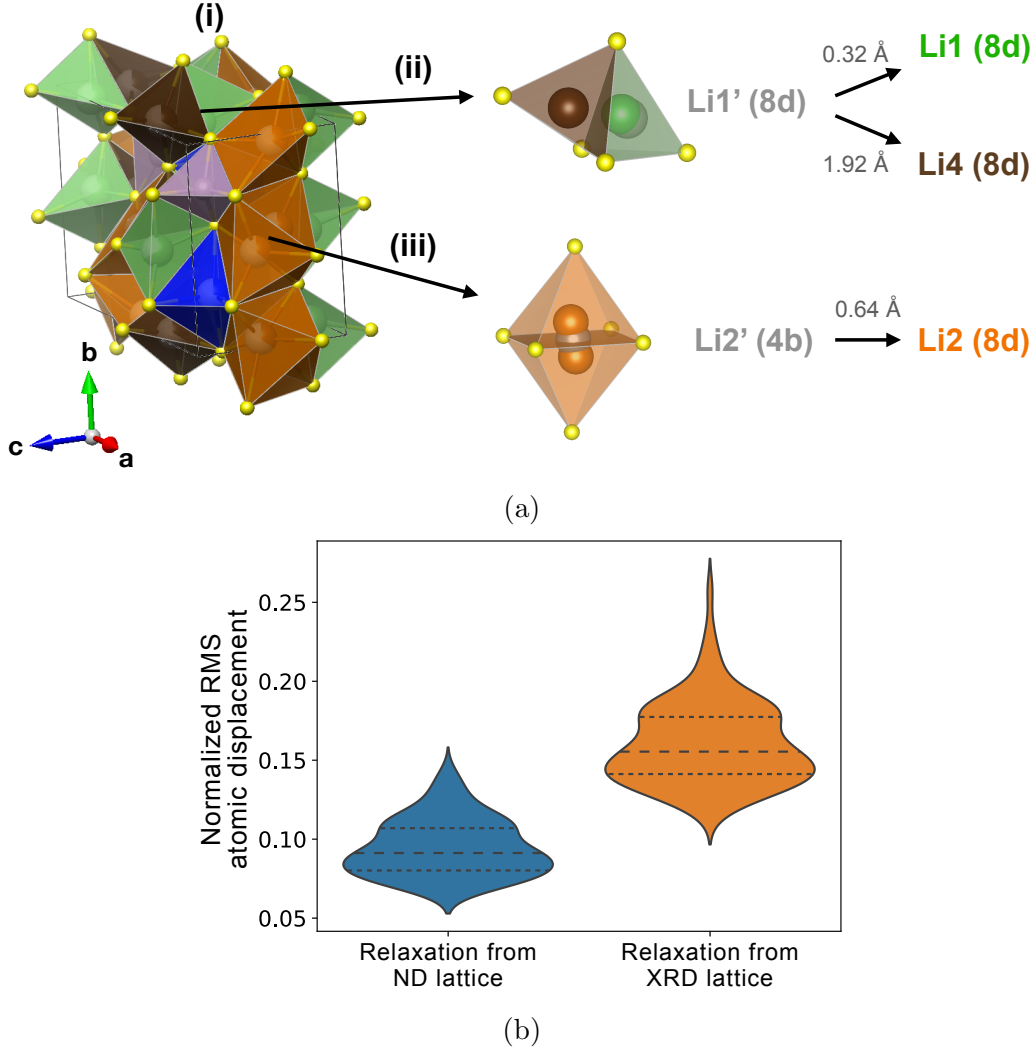


Figure 4.3: Structure of β - Li_3PS_4 . a) (i) Unit cell with Li1 (8d) (green), Li2 (8d) (orange), Li3 (4c) (blue), and Li4 (8d) (brown) sites. (ii) Splitting of Li1' (8d) (grey) to Li1 (8d) and Li4 (8d). (iii) Splitting of Li2' (4b) (grey) from square planar coordination to 5-fold coordinated Li2 (8d). b) Distributions of atomic relaxations in DFT starting from ideal ND and XRD refined structures. The extent of atomic relaxations are measured in normalized root mean squared (NRMS) atomic displacements. The dashed lines denote the 25, 50, 75 percentiles in the distributions.

other, we will refer to Li1A as Li1 (8d) and Li1B as Li4 (8d) in the following discussion. Li2' (4b) (grey in Figure 4.3a(iii)), with square planar coordination, splits into two neighboring and face-sharing Li2 (8d) sites (orange in Figure 4.3a(iii)), each with 5 fold coordination. XRD was unable to distinguish the two neighboring Li2 (8d) sites, which are only 1.3 Å apart,

and instead identified just one Li2' (4b) site.

To assess the accuracy of XRD and ND refinements of β -Li₃PS₄, we examine for all atomic positions in the DFT relaxed configurations the deviation from their XRD and ND refined sites. This is measured by calculating the normalized root mean squared (NRMS) displacement of relaxed atomic locations from the ND and XRD refined β -Li₃PS₄ lattices. The atoms of a relaxed structure are mapped back to a refined lattice site to construct the "refined" structure. The atoms of the relaxed and refined structures are then placed on an averaged lattice (in Cartesian coordinates) that minimizes the NRMS displacement, which is defined in equation 4.1, where Δx_i is the displacement of atom i between the DFT-relaxed structure and ND or XRD-refined model in Cartesian coordinates, N is the number of atoms, and V is the cell volume. The procedure described is performed using the StructureMatcher module in the pymatgen python package [50].

$$\text{NRMS displacement} = \frac{\sqrt{\sum_i^N \Delta x_i^2 / N}}{(V/N)^{1/3}} \quad (4.1)$$

In Figure 4.3b, we show violin plots of the distributions of NRMS displacement from the ND-refined structure (blue) and XRD-refined structure (orange). NRMS displacement from the ND structure is significantly smaller compared to the XRD structure, since the 3rd quartile of the ND and the 2nd quartile of the XRD distributions do not overlap (Figure 4.3b). The distribution of relaxations from the ND structure also has a smaller range, and thus less probable outliers, suggesting that the ND refinement is more accurate.

To gain insight into the physical nature of ND and XRD refined sites in β -Li₃PS₄, we examine two low-energy structures that were previously proposed as the ground state in separate first-principles studies [171, 172]. These highly similar structures are shown in Figures 4.4a and 4.4b. One contains fully occupied Li1' (8d) and Li2' (4b) sites, which yields well-ordered linear chains of Li1' and Li2' atoms along [010] and [001], and retains the Pnma symmetry of the underlying lattice—we will refer to this as the XRD ground state (XRD-GS) (Figure 4.4a). The other proposed structure is the true, lowest energy ground state in our data set, which is reported to have fully occupied Li1' (8d) and Li2' (4b) sites, but the square planar coordinated Li2' atoms are displaced off-center to a neighboring 5-fold coordination environment, characteristic of the ND refined Li2 (8d) site—we will refer to this as the ND ground state (ND-GS) (Figure 4.4b). The Li2 chain of atoms in ND-GS is staggered along [010], which leads to decreased symmetry (P2₁2₁2₁) compared to XRD-GS (Pnma). The Li site fractional occupancies of ND-GS can be described in the basis of the ND refined sites as $x_{\text{Li1}} = 1$, $x_{\text{Li2}} = 0.5$, and $x_{\text{Li3}} = x_{\text{Li4}} = 0$.

Although Li2' (4b) is located merely 0.6 Å from a neighboring Li2' (8d) site, the decrease in site energy is substantial, as ND-GS is 3.4 meV/atom lower than XRD-GS. Furthermore, when comparing phonon dispersion spectra, we find that XRD-GS is dynamically unstable

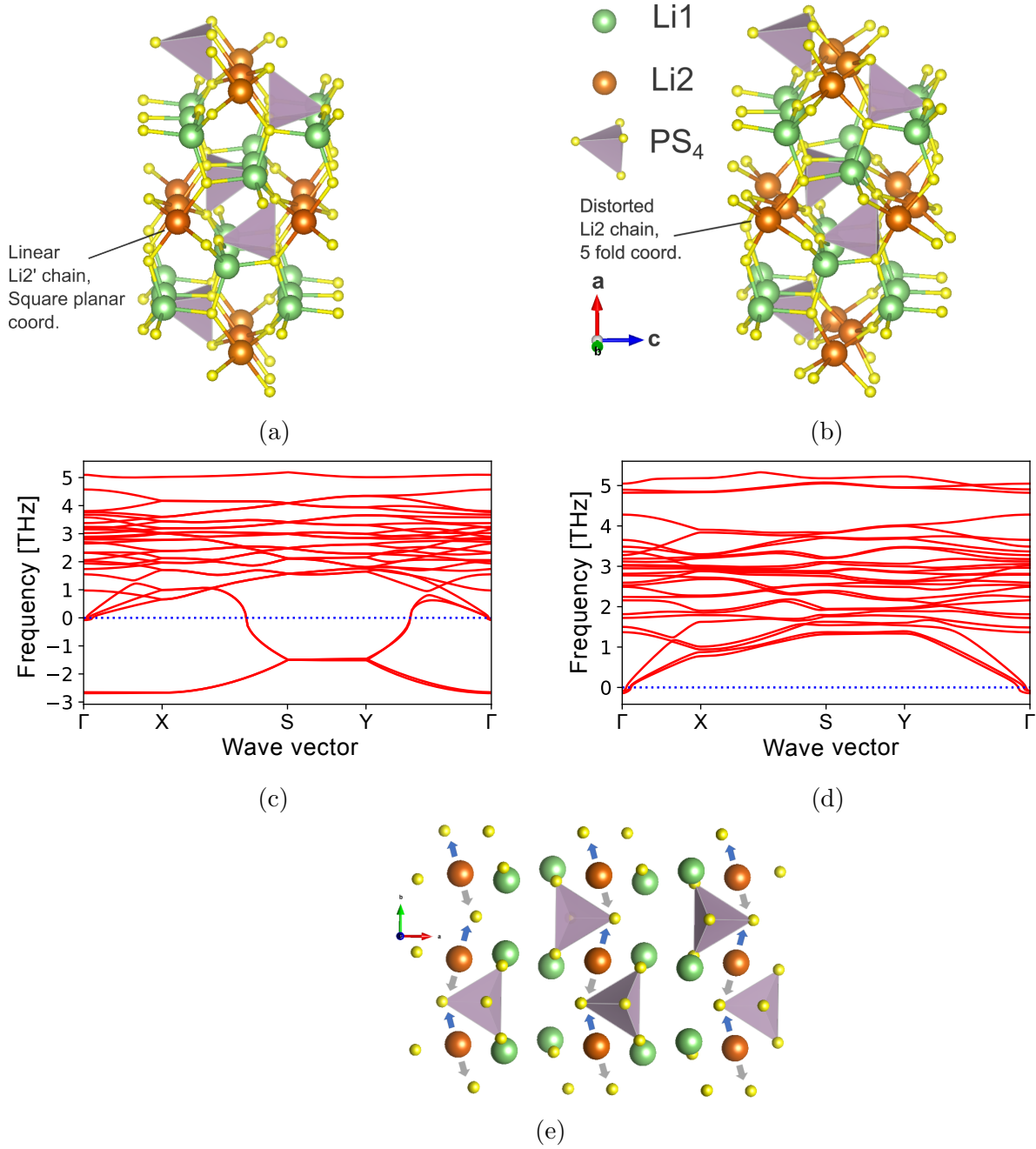


Figure 4.4: Structures of the a) XRD ground state (XRD-GS) and b) ND ground state (ND-GS) of β - Li_3PS_4 . XRD-GS contains linear ordering of $\text{Li}1$ and $\text{Li}2$ atoms along $[010]$ and $[001]$, while the ND-GS has distorted, staggered chains along $[010]$. Phonon dispersions of the c) XRD-GS and (d) ND-GS. e) Visualizing an imaginary optical mode of XRD-GS at Γ , showing collective motion of $\text{Li}2$ atoms (orange). The blue and grey arrows indicate mode displacement directions.

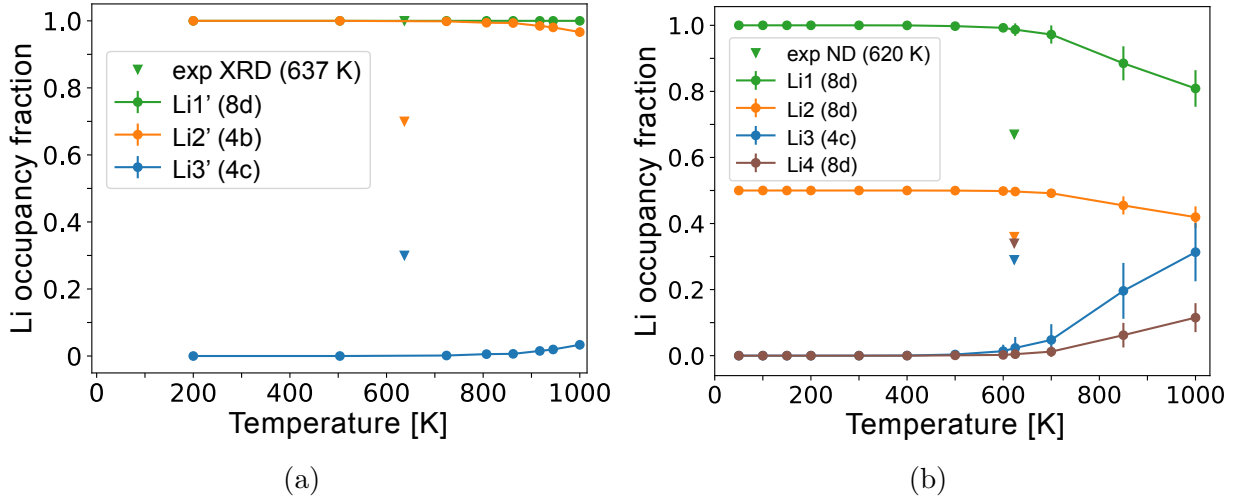


Figure 4.5: Li site fractional occupancies in β -Li₃PS₄ across temperature in MC simulations, for the a) XRD-refined lattice and b) ND-refined lattice.

with 2 nearly degenerate optical imaginary modes (Figure 4.4c), while ND-GS is dynamically stable with no imaginary modes (Figure 4.4d), agreeing well with previous reports [171]. When visualizing the XRD-GS imaginary optical modes at the Γ wave vector, we observe a collective motion of Li2' atoms (Figure 4.4e). This indicates that the XRD refined Li2' (4b) site is a high energy transition state for Li hopping between two neighboring Li2 (8d) sites. These findings highlight the importance of distinguishing fine details of the Li sublattice, as substantial differences in physical behavior can arise when site locations are slightly perturbed.

The thermodynamic disordering behavior of the XRD and ND refined structures at elevated temperature are also compared. We fit separate cluster expansions on each lattice and perform MC simulations to predict the Li site disorder as a function of temperature. In Figure 4.5, the Li site fractional occupancies across temperature are plotted. The XRD structure begins to disorder from XRD-GS at approximately 900 K, and by 1000 K changes in the Li fractional occupancies are still relatively small, yielding poor agreement with the experimental XRD refinement (Figure 4.5a). The ND structure begins to disorder from ND-GS at a lower temperature of about 600 K, and by 1000 K has significant changes in its Li fractional occupancies, highlighted by Li1 (8d) and Li3 (4c) having occupancies of 0.8 and 0.3, respectively. These values show reasonable agreement with the ND refinement at 620 K (0.7 and 0.3) (triangles in Figure 4.5b). Our simulations on both the XRD and ND structures underestimate the experimentally reported configurational disorder. However, the ND structure is predicted to have greater disorder and thus better agreement with experiment, suggesting that the ND refinement is more accurate. Specifically, introducing the Li4 (8d) site and increasing multiplicity of Li2' (4b) to Li2 (8d) generates more configurational states

that appear essential towards accurately describing the thermodynamics of this phase.

α -Li₃PS₄ structure

At high temperature ($T > 725$ K), β transforms to the orthorhombic Cmc₂m α -Li₃PS₄, increasing symmetry (Cmc₂m is a supergroup of Pnma) and slightly decreasing in density (1.6%) [155]. ND refinements report a Li sublattice containing Li1 (16h), Li2 (8e), and Li3 (4c) sites with high degree of disorder, as indicated by the isotropic Li fractional occupancies of around 0.4 [155]. An earlier refinement with XRD was deemed inconclusive, as only 1/3 Li atoms in the formula unit were refined to 1 distinct site, and there were large errors in the atomic displacement parameter (ADP) [166]. The ND refinement shows significant improvement by locating 2.9/3 Li and containing lower error in ADP [155]. Therefore, we use the ND-refined structure, which contains 3 tetrahedral Li sites over which Li atoms can disorder, to construct our cluster expansion for α -Li₃PS₄. The disordered unit cell and local Li coordination of α -Li₃PS₄ are shown in Figures 4.6a and 4.6b, respectively. We can observe that α -Li₃PS₄ contains a well-connected 1D channel of face-sharing Li1-Li2-Li1 sites along [010] (Figure 4.6b), which can be associated with fast Li-ion conduction [25]. The Li3 sites, which are edge-sharing with Li1, serve to bridge adjacent Li1-Li2-Li1 channels.

From MC simulated annealing, we find the ground state of α -Li₃PS₄ to be 3.2 meV/atom above the ground state of the β polymorph, and 8.0 meV/atom above the γ polymorph. The ground state of α -Li₃PS₄ is shown in Figure 4.6c. Li atoms only occupy the Li1 (16h) sites and form distorted linear Li chains along [010] and [001]. This indicates that Li1 (16h) sites are the most stable, and their face-sharing Li2 (8e) neighbors are higher energy intermediate sites that facilitate rapid Li diffusion. Similarly, the Li3 (4c) sites are higher energy intermediate sites that connect adjacent Li1-Li2-Li1 channels and promote 3D conductivity [155]. We note that this ground state structure contains a small monoclinic distortion (P2₁/c, lattice angle $\gamma = 86.4^\circ$) arising from slightly rotated PS₄ groups. We observe that many enumerated Li orderings of this structure contain similar symmetry-breaking lattice distortions after DFT relaxation, which indicates that the tilting of PS₄ groups can significantly affect the configurational energy landscape of this phase.

MC simulations show that Li starts to occupy Li2 (8e) sites at 200 K, and Li3 (4c) sites at 300 K (Figure 4.6d). α -Li₃PS₄ thus begins to disorder at a much lower temperature compared to β -Li₃PS₄. By 600 K, Li atoms already occupy a significant fraction of each Li site, whereas β -Li₃PS₄ only begins to disorder at this temperature. Thus, the α polymorph contains much greater configurational disorder compared to β . The high configurational entropy of α leads to the experimentally observed isotropic Li fractional occupancies of around 0.4 for each site, as reported in ND refinements at 775 K (triangles in Figure 4.6d). We note that these ND refined Li site occupancies deviate from the values obtained in our MC simulations (Figure 4.6d). This can potentially be attributed to the inability of our CE method to properly account for prominent PS₄ rotational degrees of freedom in this phase,

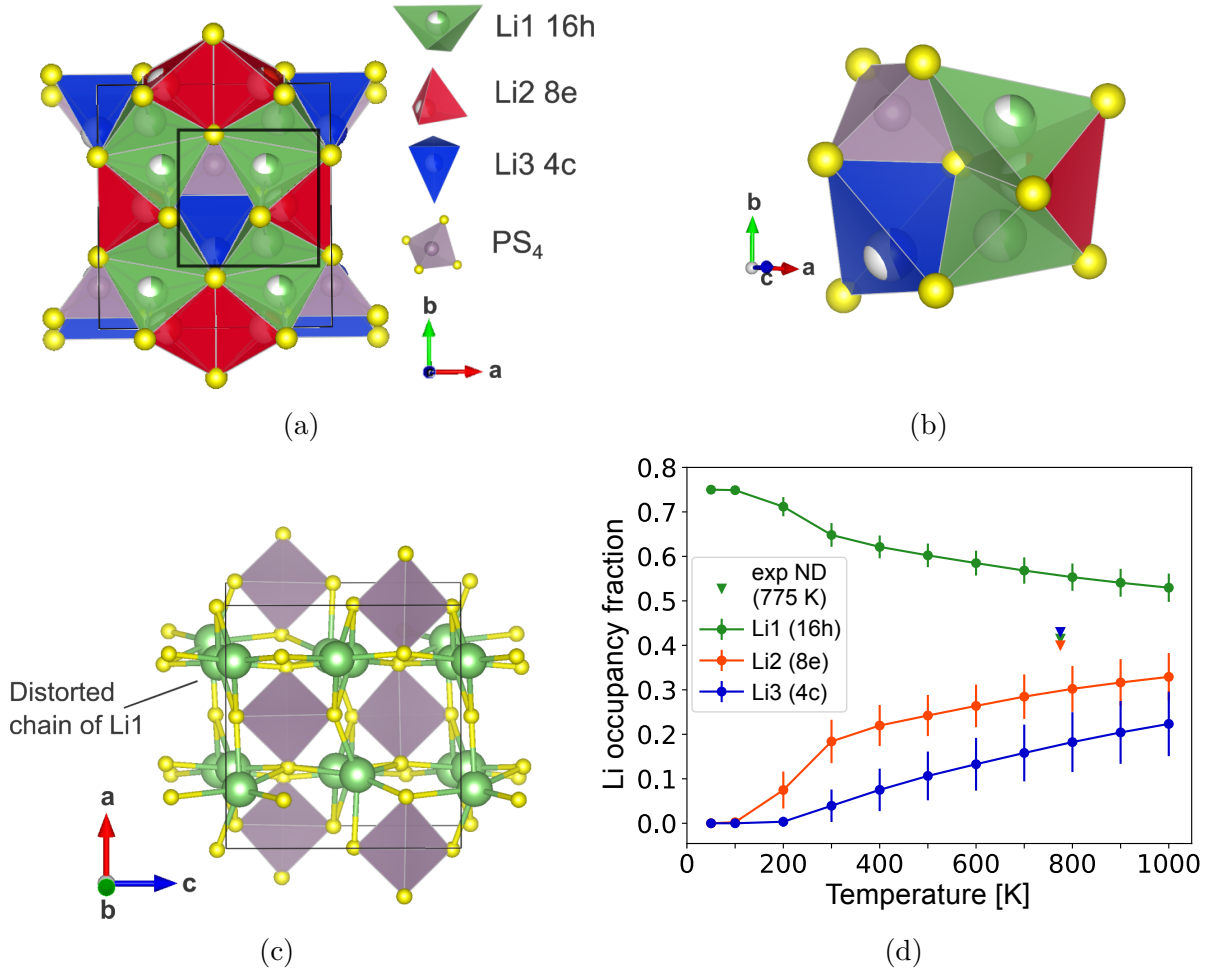


Figure 4.6: Structure of α - Li_3PS_4 . a) The unit cell with Li1 (16h) (green), Li2 (8e) (red), and Li3 (4c) (blue) sites. The boxed region is shown in greater detail in b) to display the local Li coordination. Nearest Li1 and Li2 sites are face-sharing to form a connected Li channel along [010]. Two adjacent channels are connected by Li3 sites, which are edge-sharing with Li1. c) The ground state structure with monoclinic $P2_1/c$ symmetry. Li atoms occupy only Li1 sites, forming distorted linear chains of Li along [010] and [001]. d) Li site fractional occupancies from MC simulations.

which may contribute to this CE having greater CV RMSE (4 meV/atom) compared to CE models of the other phases (Appendix Figure 4.17). More explicit treatment of strong lattice relaxations can in principle be done using adaptations of the CE method, such as the reciprocal space or rigid rotor CE formalisms [173, 174].

Li₃PS₄ phase stability

Using the structural models we validated for the Li₃PS₄ polymorphs, we assess the stability of each polymorph across temperature by calculating and comparing their free energy. In Figure 4.7, we plot the free energy of α and β relative to γ -Li₃PS₄. Since γ contains well-ordered Li, we assume it to only create vibrational entropy. At 0 K, the polymorphs ranked in order of decreasing stability are γ , β , and α . The $\gamma - \beta$ transition is predicted to occur at 370 K and the $\beta - \alpha$ transition occurs at 460 K (Figure 4.7). This order of phase transitions matches with experiments, though the predicted transition temperatures are 200 – 300 K below experimentally observed values. In experiments, it is also commonly observed that α directly transforms to γ without forming β upon cooling [152, 155], which we predict would occur at 420 K. At this temperature, the free energy differences among the polymorphs are very small (< 1 meV/atom), which helps rationalize why a direct transition can occur, especially if the transformation to γ is more kinetically favorable than forming β . We note that the r²SCAN density functional [101] is required to predict the correct order of Li₃PS₄ polymorph stability, since γ is predicted to be unstable across all temperatures when using PBE [90] (Table 4.1), which was also reported in previous first-principles calculations [158].

Table 4.1: Phase stability of Li₃PS₄ polymorphs at 0 K. Energies relative to γ -Li₃PS₄ [meV/atom] are calculated using PBE and r²SCAN functionals, with and without the zero point vibrational energy. Zero point vibrational energy is calculated using the frozen phonon method with PBE.

Polymorph	PBE	PBE+zero pt	r ² SCAN	r ² SCAN+zero pt
β	-0.3	-2.3	5.1	3.1
α	1.6	-0.1	8.4	6.6

When configurational entropy contributions are neglected (dotted lines in Figure 4.7), the free energy of α always lies above β , such that the only accessible transition is $\gamma - \beta$. This is attributed to the highly similar vibrational free energy profiles of α and β . After α begins to disorder at around 200 K, its configurational entropy increases faster than β , which drives the increased stability of α at high temperature. Furthermore, the exclusion of configurational entropy only slightly increases the $\gamma - \beta$ transition temperature to 390 K, since β has low configurational entropy at this temperature. The main source of stability for β -Li₃PS₄ is thus vibrational entropy.

To rationalize the distinctly greater vibrational entropy in β and α compared to γ -Li₃PS₄, we compare the phonon density of states (DOS) in each phase, which are shown in Figure 4.8a. β and α -Li₃PS₄ contain significantly larger DOS at 1-2 THz and around 6 THz (Figure 4.8a). The projected DOS (pDOS) shows that for all phases, the 1-2 THz region is

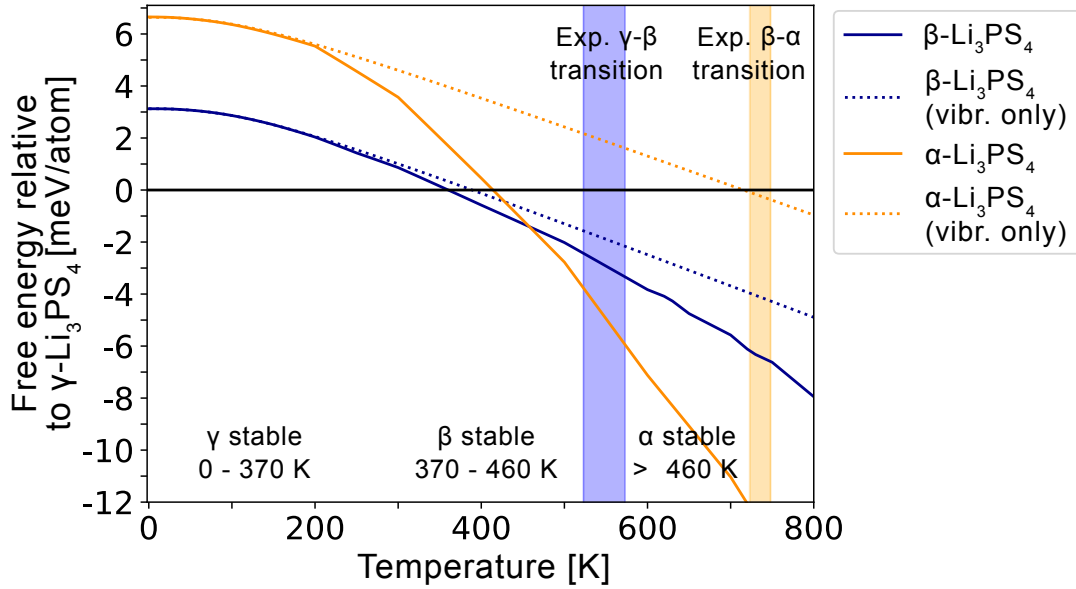


Figure 4.7: Free energy of α and β - Li_3PS_4 relative to γ - Li_3PS_4 . All experimentally reported phase transitions are observed when accounting for all free energy contributions (solid lines). γ - β transition occurs at 370 K (523 - 573 K from exp.), β - α at 460 K (723 - 748 K from exp), and α - γ at 420 K (533 K from exp upon cooling). Only the γ - β transition is observed when including only vibrational entropy contributions (dotted lines). Shaded blue and orange regions indicate experimentally observed γ - β and β - α phase transitions, respectively.

dominated by sulfur (S) modes, which are activated at low temperature around 100 K. From visualizing these modes, we observe that they mainly correspond to librations of the PS_4 groups. Furthermore, γ has no vibrations at 6 THz, whereas the high temperature phases contain significant DOS near this frequency. This frequency lies in the region between 5 to 8 THz (240 to 380 K), where β (Figure 4.8b) and α (Figure 4.8d) have roughly equal projected density of Li and S phonon modes, whereas in γ there is a significantly larger projected density of S modes than Li (Figure 4.8c). The activation of larger amplitude Li modes at around room temperature contributes to greater thermodynamic stability, and potentially towards high Li mobility in β and α - Li_3PS_4 . This finding is consistent with prior reports highlighting the relation between fast Li-ion conductivity and vibrational entropy in some superionic conductors [175].

Since the differences in low-temperature vibrational modes are likely dictated by the bonding within the S sublattice, we examine the electronic density of states (eDOS) of each ground state, which are shown in Figure 4.9. For all three polymorphs, the manifold of valence bands below the Fermi level dominantly consists of S-3p states which are spread over

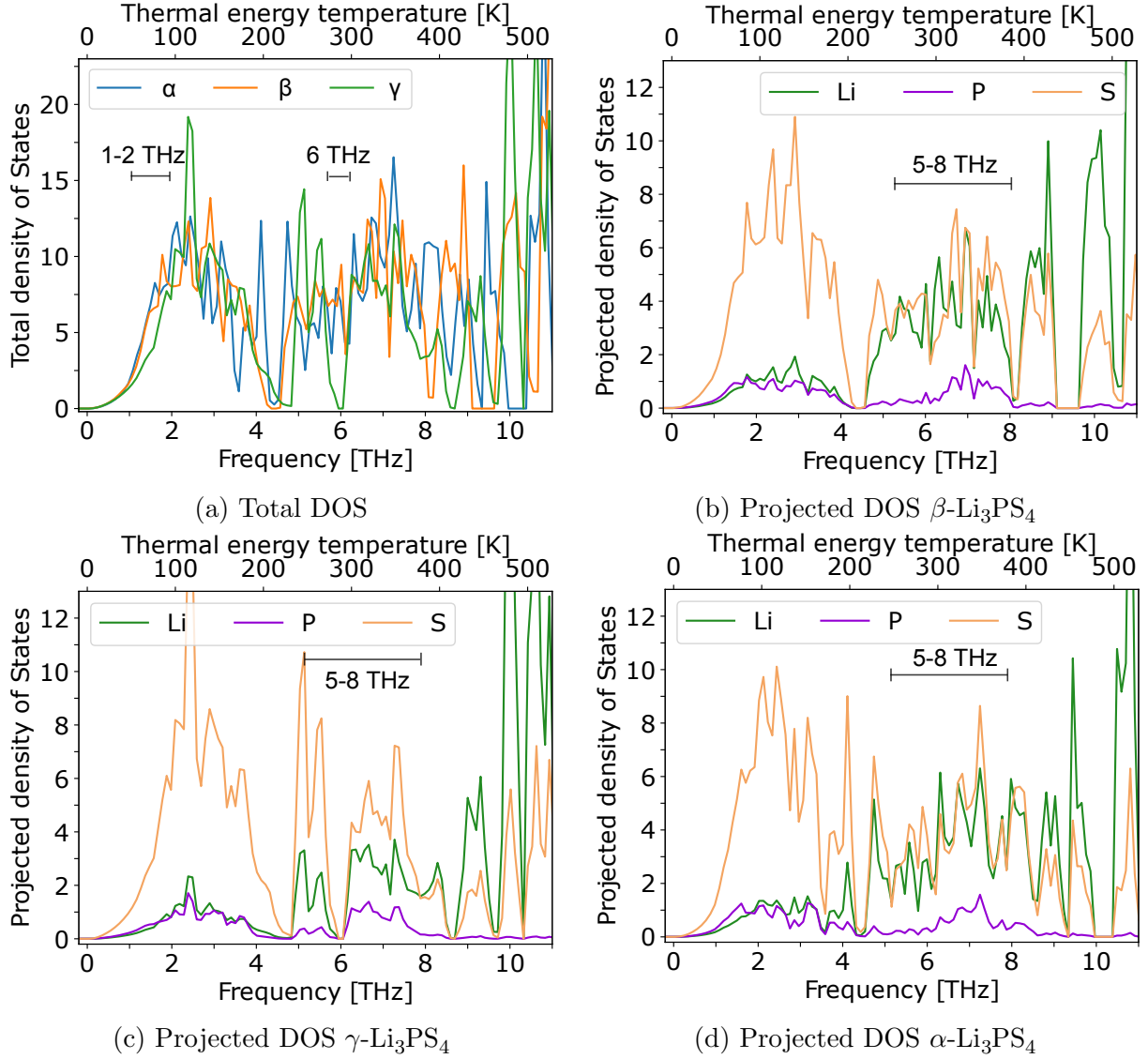


Figure 4.8: Phonon density of states. a) Total density of states (TDOS) for each Li₃PS₄ polymorph. Projected density of states (PDOS) onto Li, P, and S atoms for b) β , c) γ and d) α -Li₃PS₄ as a function of frequency and thermal energy temperature ($T = hf/k_B$), normalized per unit cell of β -Li₃PS₄ (4 formula units). γ -Li₃PS₄ contains smaller DOS at frequencies of 1-2 THz and 6 THz. The region of 1-2 THz is dominated by S modes. At 5-8 THz, γ has much larger density of S modes compared to Li, while in α and β there are equal contributions of each.

an energy range of ~ 3 eV. The relatively large band widths indicate that these states are delocalized in character and should represent long-range van der Waals interactions among

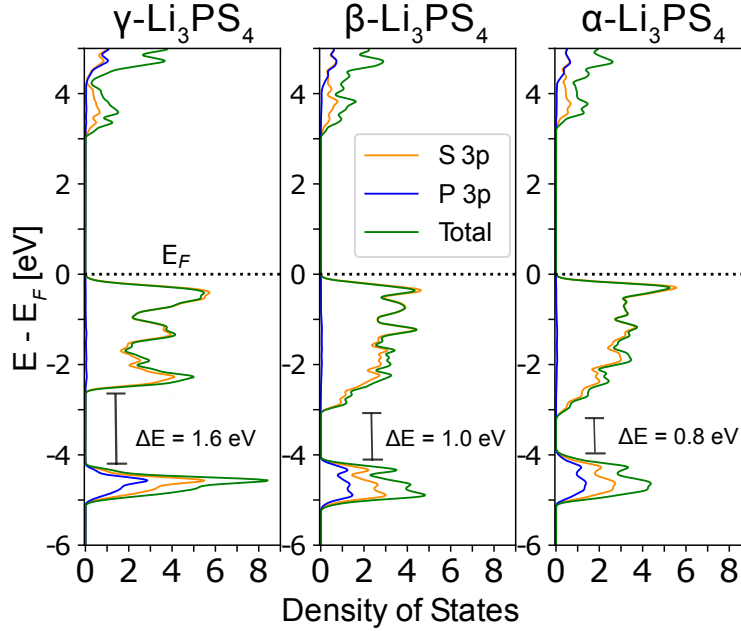


Figure 4.9: Orbital resolved electronic density of states (eDOS) of γ , β , and α - Li_3PS_4 ground state structures. Energies are referenced to the Fermi level (E_F). All phases exhibit a valence band manifold consisting of mainly S-3p states, and a lower energy core band manifold composed of hybridized S-3p and P-3p states. γ - Li_3PS_4 has a larger energy gap (ΔE) between valence and core band manifolds (1.6 eV) compared to α and β (0.8 and 1.0 eV), as well as a sharper eDOS peak in the core manifold.

S atoms in separate PS_4 units (Figure 4.9). The lower energy core band manifold is mainly composed of P-3p and S-3p states, which we attribute to P-S hybridization between the PS_4 groups. These core band states are spread over a narrower energy range of ~ 1 eV, indicating that these states are more localized.

Key differences in electronic structure are observed in the γ polymorph, which has a larger energy gap between the core and valence band states, arising from narrower band widths in the core and valence band manifolds (Figure 4.9). The core band manifold of γ also exhibits a distinctly sharp peak in the eDOS at around -4.5 eV, which results from flatter core bands. The narrower core band widths can arise from stronger hybridization of S-3p and P-3p states in neighboring PS_4 units, leading to more localization. This stronger hybridization between S and P atoms may lead to smaller interaction between S-3p states on neighboring PS_4 groups, which contributes to decreased valence band widths. It appears that the uni-directional PS_4 arrangement and denser hcp-type anion packing in γ - Li_3PS_4 [155] facilitates more isotropic and localized P-S bonding states to inhibit facile S motion. These factors would contribute to greater S sublattice stiffness and reduced density of low-frequency

S vibrational modes.

4.4 Li₇PS₆ polymorphs

Experiments show that orthorhombic LT-Li₇PS₆ (Pna2₁) is well-ordered and transforms to the higher symmetry cubic HT-Li₇PS₆ (F-43m) phase at 483 K [153]. According to XRD refinements, HT-Li₇PS₆ contains a disordered Li sublattice with one distinct Li1 (48h) site, which is corner-sharing with PS₄ units and face-sharing with its nearest Li1 neighbor [153]. No ND refinement has yet been reported on the HT-Li₇PS₆ phase; however, ND refinements have been reported for a Cl-doped analogue Li₆PS₅Cl [160]. An additional Li2 (48h) site was identified in Li₆PS₅Cl that is edge-sharing with PS₄ units, and face-sharing with its nearest Li1 and Li2 neighbors to form a cage-like Li substructure (Figure 4.10b), while the sublattices of the PS₄ and isolated S atoms are identical. Since Cl substitutes a fraction of S atoms without causing much change in lattice parameters, we presume that the Li sites in the doped and pristine phases are very similar and comparable. [160].

As done with the β -Li₃PS₄ phase, we compare the NRMS atomic relaxations (Equation 4.1) of the DFT relaxed configurations starting from either the ND or XRD refined atomic positions of HT-Li₇PS₆, the distributions of which are plotted in Figure 4.10c. We observe that there is a much smaller NRMS atomic displacement from the ND-refined lattice (mean of 0.12) compared to the XRD-refined lattice (mean of 0.19), indicating that the ND positions for Li are closer to the energy minimum.

We model Li-vacancy disorder in HT-Li₇PS₆ by fitting a CE using the ND refinement of Li₆PS₅Cl containing Li1 (48h) and Li2 (48h) sites, with all Cl atoms replaced by S atoms. Through MC simulated annealing, we identify a ground state ordering, shown in Figure 4.10d, which contains 6 Li atoms in the unit cell (out of 28 Li) occupying Li2 sites, as evidenced by their edge-sharing with PS₄ (orange in Figure 4.10d). The prominence of Li2 as a stable site in the ground state provides further evidence that the structure refined by ND is more accurate and that the Cl doping does not influence the location of Li sites.

We perform MC simulations to predict the Li site occupancies as a function of temperature, which are plotted in Figure 4.11. The fraction of Li occupying Li1 is greater at all simulated temperatures, in reasonable agreement with Li site occupancy of Li₆PS₅Cl measured by ND at ambient temperature [160]. The preference of Li going to Li1 sites could be explained by its corner-sharing with PS₄, which can reduce the repulsive interaction with P cations compared to the edge-sharing Li2 sites [11].

The HT-Li₇PS₆ ground state structure was found to be 10.4 meV/atom more stable than the ordered LT-Li₇PS₆ structure proposed by XRD, suggesting that the XRD refinement for LT-Li₇PS₆ may not be accurate [153]. To seek a more representative LT-Li₇PS₆ structure, we perturb its XRD refined structure through an AIMD simulation. The structure is heated

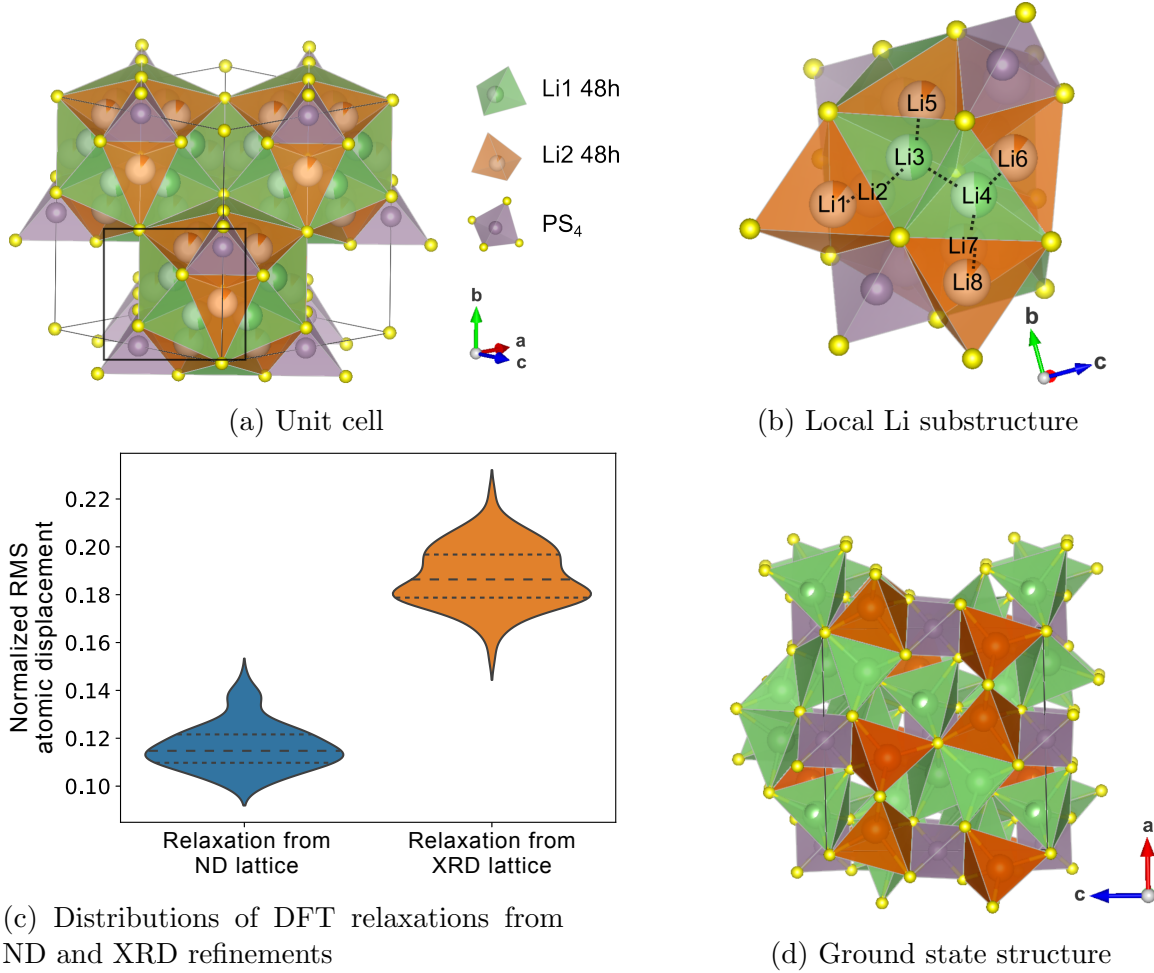


Figure 4.10: Structure of HT-Li₇PS₆. a) The unit cell (F-43m) with Li1 (48h) (green) sites that are corner-sharing with PS₄, and Li2 (48h) (orange) sites that are edge-sharing with PS₄. The boxed region containing a single cage-like Li substructure is shown in greater detail in b), which displays the local Li site coordination. Dotted lines connect face-sharing Li atoms. c) Violin plots displaying distributions of normalized root mean squared (NRMS) atomic displacements of DFT relaxed configurations from ND and XRD refinements. Dashed lines denote division between data quartiles. d) Ground state structure of HT-Li₇PS₆, containing 6 occupied Li2 (48h) sites (orange).

to 800 K for 2 ps, held for 30 ps, and annealed to 100 K for 20 ps. Samples along the AIMD trajectory are relaxed, from which we identify a significantly more stable structure that is 1.2 meV/atom below the HT-Li₇PS₆ ground state. This new LT-Li₇PS₆ ground state (shown in Figure 4.12a) has a slight monoclinic distortion (lattice angle $\beta = 91^\circ$), resulting from a small relaxation of the PS₄ units away from a parallel arrangement, and some Li are

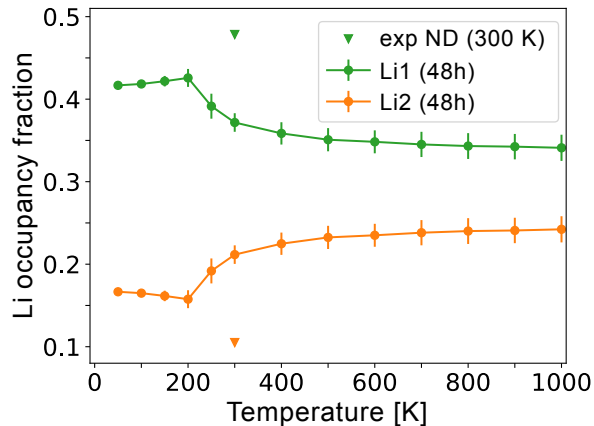


Figure 4.11: HT-Li₇PS₆ Li site occupancy fractions across temperature. The reported experimental occupancies (triangles) were measured with ND on Li₆PS₅Cl at 300 K, and are scaled by 7/6 to account for the different Li stoichiometry, compared to Li₇PS₆.

shifted to new coordination environments. We also find a large spread of energies among the sampled structures that were relaxed (Figure 4.12b), indicating that LT-Li₇PS₆ is likely configurationally disordered as well. We leave further analysis of the LT-Li₇PS₆ Li sublattice for future investigation. But our investigation confirms that, with our reassignment of the Li sites, LT-Li₇PS₆ is the ground state at low temperature.

Using our newly proposed ground states, we predict the phase stability of the Li₇PS₆ polymorphs at finite temperatures. In Figure 4.13, we plot the free energy of HT-Li₇PS₆ relative to LT. HT-Li₇PS₆ becomes stable at 270 K, with the majority of its stabilization relative to LT-Li₇PS₆ arising from configurational entropy contributions (Figure 4.13). Our predicted transition temperature is roughly 200 K below its experimentally observed value of 480 K. The likely cause for this understabilization of LT-Li₇PS₆ is that we may not have identified its true ground state yet, and that it contains significant configurational entropy contributions that have been neglected from our model because of the lack of a precise Li sublattice.

4.5 Li₇P₃S₁₁

Li₇P₃S₁₁ crystallizes in the low symmetry P-1 space group, and is composed of PS₄ and P₂S₇ units. In both XRD and ND refinements, the Li sublattice is ordered with 7 distinct sites [167, 154]. However, each refinement reports Li atoms occupying a different set of sites. From our DFT calculations, we find that the XRD refined structure is substantially more stable than the ND refined structure by 9 meV/atom. A more recent first-principles study by Chang and coworkers proposed a disordered Li sublattice with 8 additional Li sites,

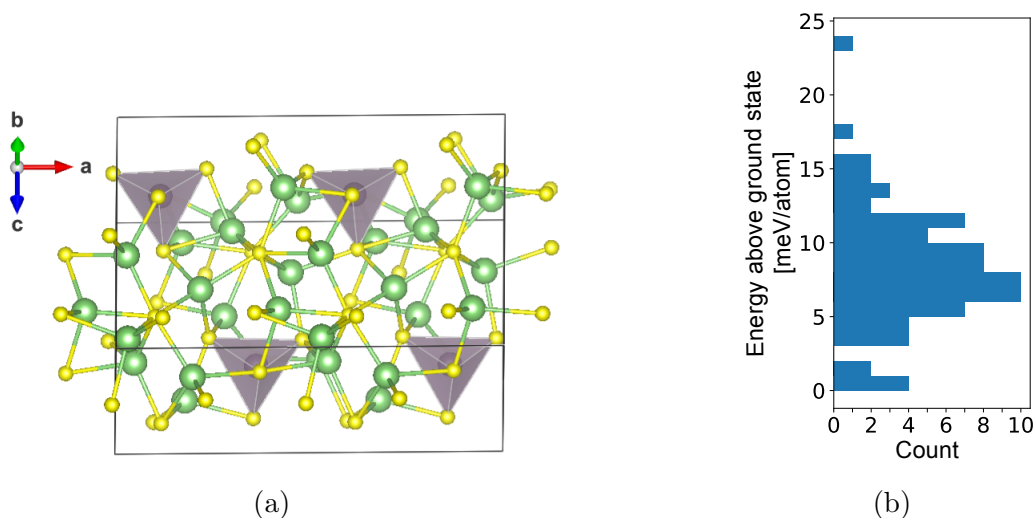


Figure 4.12: Structure of LT-Li₇PS₆. a) The ground state structure identified from AIMD simulations. PS₄ units relax slightly away from a parallel arrangement, contributing to a slight monoclinic distortion, with unit cell angles: $(\alpha, \beta, \gamma) = (90.0, 91.0, 90.0)$. b) Histogram of energies above ground state for structures sampled along the AIMD trajectory. Reported energies are calculated from ionic relaxations using the PBE functional.

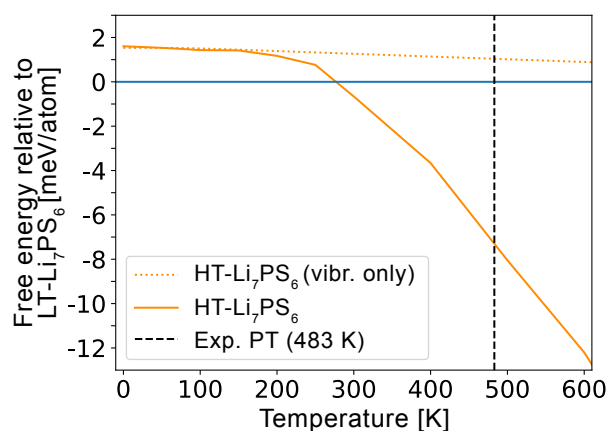


Figure 4.13: Free energy of HT-Li₇PS₆ relative to LT-Li₇PS₆. Phase transition from LT to HT is predicted at 280 K, compared to 483 K from experiment.

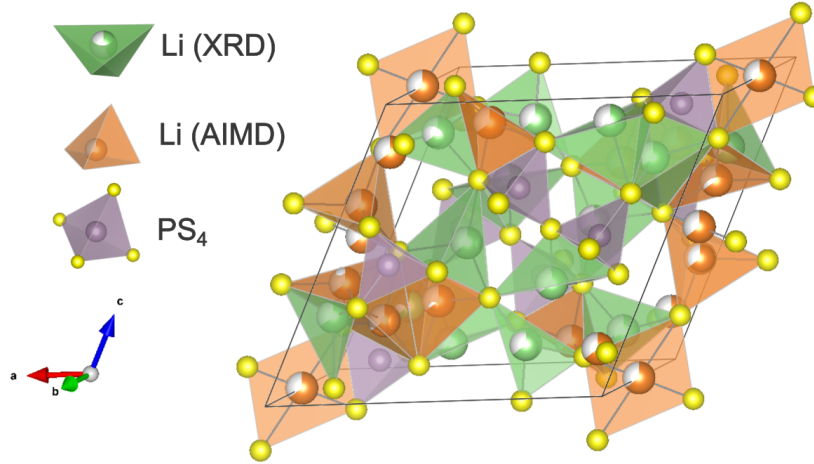


Figure 4.14: Disordered unit cell of $\text{Li}_7\text{P}_3\text{S}_{11}$ with 7 distinct Li sites identified from XRD (green) and 8 distinct sites identified from AIMD simulations (orange).

identified from AIMD simulations [168]. The authors enumerated structures based on the disordered Li sublattice and reported a ground state that is 0.8 meV/atom more stable than the XRD-refined structure, using the PBE functional. This value is qualitatively consistent with our calculations using r^2SCAN , which yield an energy difference of 1.0 meV/atom.

We train a CE on the previously reported disordered $\text{Li}_7\text{P}_3\text{S}_{11}$ lattice containing 15 distinct Li sites, which are a sum of the sites identified from XRD and AIMD. The unit cell is shown in Figure 4.14, from which we can observe that the possible Li sites include a range of planar and tetrahedral coordination environments with varying degrees of distortion. Through MC simulated annealing, we uncover a new ground state ordering that is 1.0 meV/atom more stable than the ground state previously proposed by Chang and coworkers [168].

Since crystallographic refinements have not reported the existence of configurational disorder in this phase, it is important to quantify the degree of disorder, and compare this with other superionic conductors [154, 167]. To that end, we calculate the configurational entropy as a function of temperature with MC simulations for $\text{Li}_7\text{P}_3\text{S}_{11}$, and compare it to that of $\alpha\text{-Li}_3\text{PS}_4$, $\beta\text{-Li}_3\text{PS}_4$, and $\text{HT-Li}_7\text{PS}_6$, which are plotted in Figure 4.15. $\text{Li}_7\text{P}_3\text{S}_{11}$ (red) is predicted to contain significant configurational entropy that is greater than $\beta\text{-Li}_3\text{PS}_4$ (light blue), and lower but comparable to $\alpha\text{-Li}_3\text{PS}_4$ (dark blue) and $\text{HT-Li}_7\text{PS}_6$ (green). This result corroborates the additional Li sites in the disordered Li sublattice identified from AIMD [168]. We remark that all superionic conductors in this phase space contain significant configurational entropy that is of the same order of magnitude, indicating a potential correlation between superionic conductivity and configurational entropy.

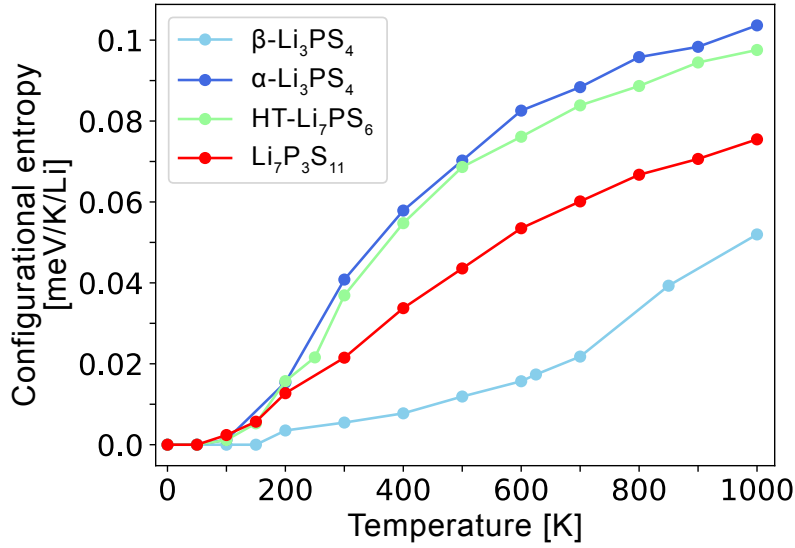


Figure 4.15: Configurational entropy in the disordered superionic conductors α -Li₃PS₄, β -Li₃PS₄, HT-Li₇PS₆, and Li₇P₃S₁₁ phases, normalized per Li atom.

4.6 Discussion

Through first-principles calculations, we derive a phase diagram of the Li₂S-P₂S₅ system that recovers well-established experimental trends such as polymorph phase transitions in Li₃PS₄ and Li₇PS₆, and the instability of Li₇P₃S₁₁ at high temperature. All superionic conductors are predicted to be metastable at room temperature. An accurate assessment of the configurational entropy required precise information on the possible Li sites in these structures. We find that ND refinements tend to contain more accurate details about Li sites and degree of disorder, compared to XRD refinements. Our calculations show that these details from ND are critical towards predicting physically accurate dynamical stability and thermodynamic behavior.

We predict that all superionic conductors in this space are metastable at ambient temperature, in agreement with previous studies [10, 151, 155, 150, 161, 164]. Specifically, α -Li₃PS₄, β -Li₃PS₄, HT-Li₇PS₆, and Li₇P₃S₁₁ have energies above the hull (E_{hull}) of 4, 1, 12, and 4 meV/atom at 300 K, respectively. These values are well within the range of energy for which metastability is observed in the large-scale study on metastability by Sun et al., who found that metastable inorganic sulfide compounds in the inorganic crystal structure database (ICSD) yielded a median E_{hull} of 9.7 meV/atom and a 90th percentile E_{hull} of 45.3 meV/atom at 0 K [169]. HT-Li₇PS₆ is the only superionic conductor in this system with greater E_{hull} at 0 K (16 meV/atom) than the median value, and all are below the 90th percentile value found by Sun et al. While low E_{hull} has been suggested to be a required criterion

for metastability, Sun et al. point out that it is not sufficient to guarantee metastability. However, the low E_{hull} for these phases is certainly consistent with their accessibility.

Vibrational and configurational sources of entropy are shown to be crucial towards describing phase stability trends. Among the Li_3PS_4 polymorphs, the superionic conductors α and β have distinctly greater vibrational entropy compared to γ , which has low Li conductivity. We attribute this to the softness of the anion sublattice, as α and β - Li_3PS_4 contain significantly more low-frequency S vibrational modes, mainly corresponding to librations of the PS_4 group. The potential electronic origin of the stiffer anion sublattice in γ - Li_3PS_4 lies in the stronger hybridization of the P-3p and S-3p states near the Fermi level. We postulate that these subtle differences in longer range binding between PS_4 units are the reason why a meta-GGA level of theory is required to predict the correct order of Li_3PS_4 polymorph stability, as the SCAN family of density functionals have been shown to be superior at capturing medium-range van der Waals interactions [97, 98]. These findings can potentially motivate new design principles for novel superionic conductors based on features of the phonon and electronic band structure [175].

Configurational sources of entropy are also essential towards describing phase stability trends. The polymorphic phase transitions involving α - Li_3PS_4 and HT- Li_7PS_6 can only be predicted when accounting for configurational disorder, which in turn requires accurate assessment of possible sites that Li can access. Furthermore, all superionic conductors in this phase space generate a significant amount of configurational entropy. β - Li_3PS_4 has the lowest configurational entropy, and coincidentally its bulk ionic conductivity has been reported to be low ($8.9 \cdot 10^{-3}$ mS/cm), with only its nanoporous form having high Li conductivity (0.16 mS/cm) [156]. The high temperature α polymorph has considerably greater configurational entropy and room temperature Li conductivity of ~ 2 mS/cm [159]. Meanwhile, the γ polymorph has the lowest ionic conductivity and contains no configurational disorder. This observation suggests an inherent correlation between fast Li mobility and high configurational entropy.

This trend is observed in many other systems as well. We show that HT- Li_7PS_6 has high configurational entropy, comparable to α - Li_3PS_4 , and it is experimentally shown to have greater Li conductivity than LT- Li_7PS_6 [161]. This trend is not unique to sulfide superionic conductors, as the oxide garnet $\text{Li}_7\text{La}_3\text{Zr}_2\text{O}_{12}$ (LLZO) has a low-temperature ordered tetragonal phase with low Li conductivity, and a high-temperature disordered superionic conductor with increased cubic symmetry [176]. We observe that superionic conductors tend to be high temperature polymorphs with increased symmetry arising from the configurational disorder. These phases must be entropically stabilized at high temperature, which lends further support that high entropy is favorable towards achieving a superionic conducting state.

We can rationalize the origin of high configurational entropy by analyzing Li site energies. β - Li_3PS_4 and its higher symmetry α - Li_3PS_4 polymorph are ideal systems to compare, as they have the same number of Li atoms and Li sites per unit cell. A first order approximation for

the Li site energy is the site’s effective cluster interaction (ECI) energy (J_{ECI}) obtained from the CE using an orthonormal basis, which are plotted in Figure 4.16a. It can be shown from the cluster decomposition framework that this is a unique and physical value to describe the energy of Li occupying a particular site [177]. This approximation can be justified by the observation that single-site ECI tend to be much larger in magnitude than the multi-site pair and triplet ECI (Appendix Figure 4.18); single-site ECI thus carry most of the weight in the total energy. We also calculate a site energy normalized by its multiplicity ($\hat{J}_{ECI}$), which would provide a better estimate of the energy contribution of the site per unit cell. This is described in Equation 4.2, where M is the multiplicity of a distinct Li site and N is the total number of Li sites per unit cell.

$$\hat{J}_{ECI} = J_{ECI} \cdot \frac{M}{N} \quad (4.2)$$

In Figure 4.16b, we plot the standard deviation of $\hat{J}_{ECI}$ in each Li_3PS_4 phase, showing that α contains a significantly smaller spread of $\hat{J}_{ECI}$ (8 meV) compared to the β polymorph (41 meV). Thus, in α the Li atoms will have a comparable energetic preference for occupying all sites. Many configurations will then have similar energy, which contributes towards its greater configurational entropy. The larger Li site energy spread in β means that Li atoms will tend to order by occupying the lowest energy sites and thus have smaller configurational entropy.

The potential connection between high Li mobility and configurational entropy suggests that increasing disorder should be a promising strategy to design superionic conductors. Indeed, there have been many examples where aliovalent cation or anion doping improves Li conductivity and enables room temperature phase stability. These include adding Si into Li_3PS_4 to form $\text{Li}_{3.25}\text{P}_{0.75}\text{Si}_{0.25}\text{S}_4$ in the β - Li_3PS_4 structure [158], adding Cl or other halogen atoms (X) to Li_7PS_6 to form $\text{Li}_6\text{PS}_5\text{X}$ in the HT- Li_7PS_6 structure [160, 163, 162], and doping Al or Ga into $\text{Li}_7\text{La}_3\text{Zr}_2\text{O}_{12}$ to stabilize its high-temperature cubic structure [178]. In some cases, it has been claimed that inducing alkali-ion vacancies even without the presence of dopants can stabilize superionic conducting polymorphs, such as the high temperature Na_3PS_4 polymorph [179]. Our MC simulations have shown that the disorder arising from only Li and vacancies can generate substantial configurational entropy and that this entropy can dictate phase stability trends.

Previous studies have also shown that adding dopant species can alter the Li site energy landscape to facilitate dramatic improvements in ionic conductivity. Zeng and co-workers demonstrated that high-principal element cation doping can boost ionic conductivity by orders of magnitude [180]. Through first principles calculations, they showed that distortions to Li environments introduced by dopants can lead to Li site energy levels that are more closely spaced, promoting Li-ion percolation. It is possible that the soft degrees of freedom for libration of the PS_4 units as seen in several polymorphs further generates the distribution of temporary site energies which leads to low energy barrier percolation pathways [181].

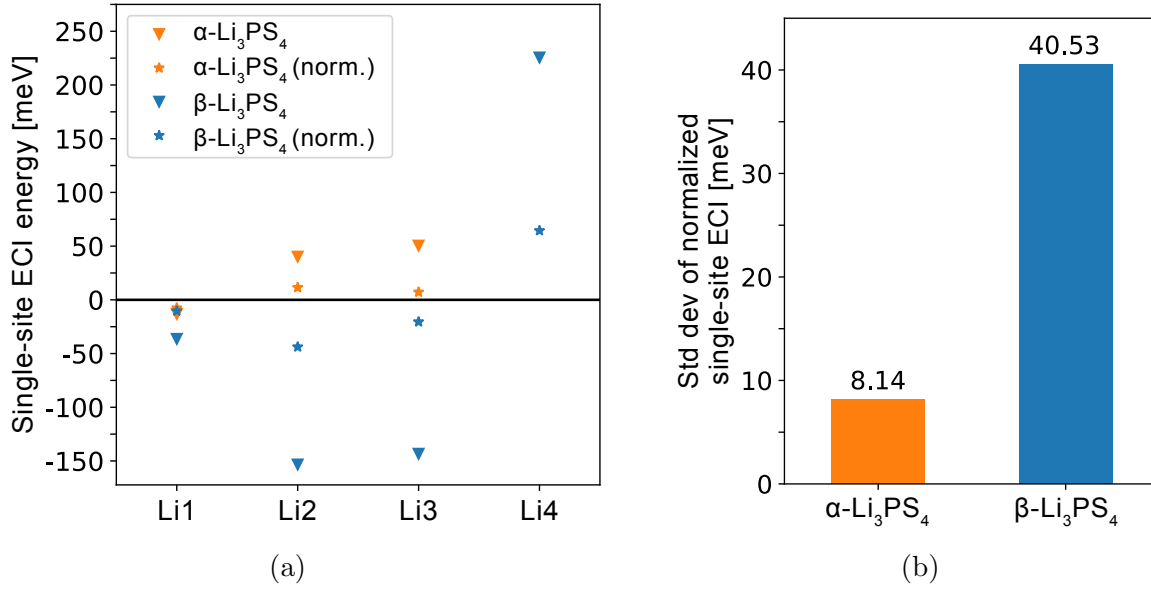


Figure 4.16: Comparing Li site energies in α and β - Li_3PS_4 polymorphs. a) ECI energies corresponding to single-site functions in the CE (J_{ECI} , denoted by triangles), and ECI energies normalized by site multiplicity ($\hat{J}_{ECI}$, denoted by stars). In β , the sites are Li1 8d, Li2 8d, Li3 4c, and Li4 8d. Positive values correspond to an increase in energy from Li occupying a site. In α , the sites are Li1 16h, Li2 8e, and Li3 4c. b) Standard deviation of $\hat{J}_{ECI}$.

Similarly, Wang and co-workers found that adding Br into Li_3YCl_6 to form $\text{Li}_3\text{YBr}_{1.5}\text{Cl}_{4.5}$ introduced a larger variety of closely spaced octahedral Li site energy levels, leading to a lower order-disorder transition temperature and increased Li conductivity [182]. These previous studies highlight that engineering a more uniform Li site energy landscape can facilitate more facile Li-ion migration, since there is a greater probability that neighboring sites are close in energy, which in turn can lead to lower energy barriers for Li hopping between them. This is not a sufficient condition for high conductivity as the component of the migration energy that is independent of the site energy also needs to be small. We can synthesize this with our finding that smaller variance in Li site energies necessarily leads to greater configurational disorder as well, which illustrates why the phenomena of superionic conductivity and high configurational entropy should be intrinsically linked. This rationalizes why tuning the Li site energy landscape through introducing dopants and Li off-stoichiometry has been, and should continue to be, an essential design principle for discovering superionic conductors with improved Li conductivity and thermodynamic accessibility.

Although we have predicted the phase stability trends and rationalized them on the basis of configurational and vibrational contributions, our predicted phase transition temperatures tend to underestimate experimentally observed values by about 200 K. The phase stability

trends in this system are described on a rather fine energy scale on the order of 10 meV/atom. Subtle changes such as hypothetically shifting the free energy curve of β -Li₃PS₄ up by 3 meV/atom can already increase the $\gamma - \beta$ phase transition temperature to its experimentally observed window. These small energy differences are easily within the bounds of error in our computational techniques.

Specifically, it is known that semi-local density functionals, such as the PBE and r²SCAN functionals, struggle to capture long-range dipole-induced dipole interactions [97], which are likely to be prominent within the S sublattice in these materials. The error from CE configurational energies is compounded onto the DFT error since the CEs are trained on DFT data. On the basis of CV RMSE, CE energy error ranges from 1 to 5 meV/atom, depending on the phase. Furthermore, anharmonic corrections to phonon calculations may yield key differences in the band dispersion and resulting vibrational free energy, as previously demonstrated in the sodium thiophosphate (Na₃PS₄) analogue [62]. The facile and long-range nature of Li hopping modes are a potential source of anharmonicity in superionic conductors.

4.7 Conclusion

A phase diagram of the pseudo-binary Li₂S-P₂S₅ system has been constructed from first-principles calculations. Well-established experimental trends, such as the phase transitions among Li₃PS₄ and Li₇PS₆ polymorphs, and the metastability of Li₇P₃S₁₁ are recovered. The superionic conductors α -Li₃PS₄, β -Li₃PS₄, HT-Li₇PS₆, and Li₇P₃S₁₁ are all predicted to be metastable at 300 K ($E_{\text{hull}} = 4, 1, 12, \text{ and } 4$ meV/atom, respectively), but thermodynamically accessible. We find that accounting for both vibrational modes and Li configurational disorder are essential for describing phase stability trends. Physically accurate evaluation of configurational entropy could only be made after clarifying the details of the Li sublattices in the superionic conductors. We demonstrate that these phases all contain significant configurational entropy, which suggests a correlation between high Li configurational entropy and fast Li conduction. Engineering a more uniform Li site energy landscape through doping and tuning the Li content should thus be essential design principles for discovering novel superionic conductors with improved thermodynamic stability and Li conductivity at ambient temperature.

4.8 Methods

All electronic structure calculations were performed using the Vienna ab-initio simulation package (VASP) [70, 183]. For the ground state structures of each phase, ionic relaxations were performed with 1e-05 eV convergence in the total energy and 1e-02 eV/Å in the forces, initially using the generalized gradient approximation (GGA) functional as parameterized by Perdew, Burke, and Ernzerhof (PBE) [90], projector augmented wave (PAW) pseudopotentials [80], and a plane-wave basis set with an energy cut-off of 520 eV. The GGA-converged

structure was further relaxed with the meta-GGA r^2 SCAN functional [101], with a k-point spacing dependent on the band gap of the PBE calculation, a scheme proposed by Kingbury and co-workers [102]. The final reported formation energies were obtained from a static calculation with denser k-point spacing of $0.2 \text{ \AA}^{-1}$. To plot the electronic density of states (eDOS), we perform another static calculation using r^2 SCAN with stricter electronic convergence ($1e-07 \text{ eV}$) and the eDOS was calculated at 2000 energy points. All structure generation, manipulation, and symmetry analysis was performed using `pymatgen`. [50]

Cluster expansion (CE) construction and Monte Carlo (MC) sampling were performed with the SMOL Python package [184]. CEs were trained on superstructures relaxed using the PBE functional only, to limit the computational cost. It has been previously shown that similar schemes of mixing levels of theory can yield physically accurate phase diagrams [185]. We simultaneously parameterize the CE with an additional electrostatic term to describe long-range Coulomb interactions. To that end, we fit an effective dielectric constant (ϵ) that screens the ionic electrostatic energy, which was calculated from the bare Coulomb interaction between idealized Li^+ , P^{5+} , and S^{2-} point charges with the Ewald summation method as implemented in `pymatgen` [50]. CE fitting was performed in a piece-wise manner, where the initial fit only trained the point correlation functions and effective dielectric constant (ϵ), using L_2 norm penalized linear regression [53]. The residual of the initial fit was used to train the pairs and higher-order effective cluster interactions (ECI) with penalization of the L_1 norm to promote a sparse solution [51, 52]. We observed that this method yields improved fit stability and a more physical ϵ , which is attributed to decreased regularization of ϵ [35]. The optimal regularization hyperparameters were chosen to minimize the cross-validation (CV) root mean squared error (RMSE), with the condition that the training set RMSE lies within the standard deviation of the CV RMSE, to mitigate over-fitting. MC sampling was performed in supercells for each phase in the canonical ensemble, with decreasing temperatures starting at 1000 K. Supercells were constructed to contain at least 200 Li sites and have similar lattice parameters. At least 40000 MC passes were performed at each temperature. To calculate configurational free energy, the average internal energy ($\langle E \rangle$) at each temperature was integrated over inverse thermal energy ($\beta = \frac{1}{kT}$) (Equation 4.3).

$$\beta F_{\text{config}}(T) = \beta F_{\text{config}}(T = T_0) + \int_{\beta_0}^{\beta} \langle E \rangle d\beta \quad (4.3)$$

New ground states were found from simulated annealing, using a similar procedure of canonical MC sampling at decreasing temperature, but with unit cells and smaller supercells.

Harmonic phonon calculations were performed on the ground state of each phase, with the frozen phonon method using Phonopy and VASP [59]. Structures were relaxed with PBE to a stricter convergence criteria of $1e-7 \text{ eV}$ in energy and $1e-3 \text{ eV/\AA}$ in the forces. Atomic displacements were generated on supercells, which were created such that each lattice parameter is greater than $12 \text{ \AA}$ and nearly equal to each other. For P_2S_5 only, we calculate the phonon properties using density functional perturbation theory (DFPT) as implemented

in VASP [186], because we observed that the frozen phonon method yielded many imaginary modes, which we attribute to strong anharmonicity. Non-analytical correction to modes near the Γ wave vector was performed by incorporating the dielectric properties, to account for longitudinal optical and transverse optical (LO-TO) mode splitting in polar ionic materials in the long wavelength limit [141]. Dielectric permittivity and Born effective charge tensors were computed with DFPT [186], using a denser reciprocal space discretization of $0.125 \text{ \AA}^{-1}$ to ensure convergence of dielectric properties [187].

4.9 Appendix

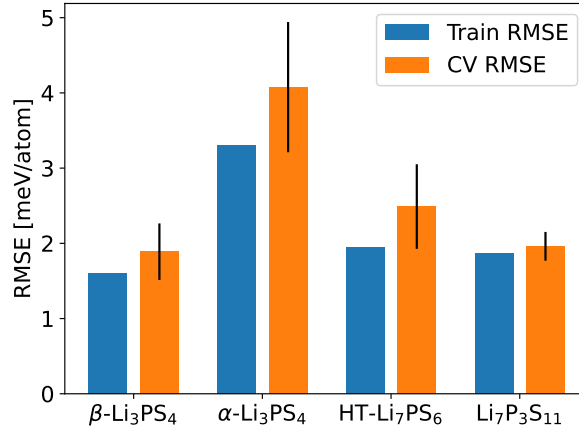
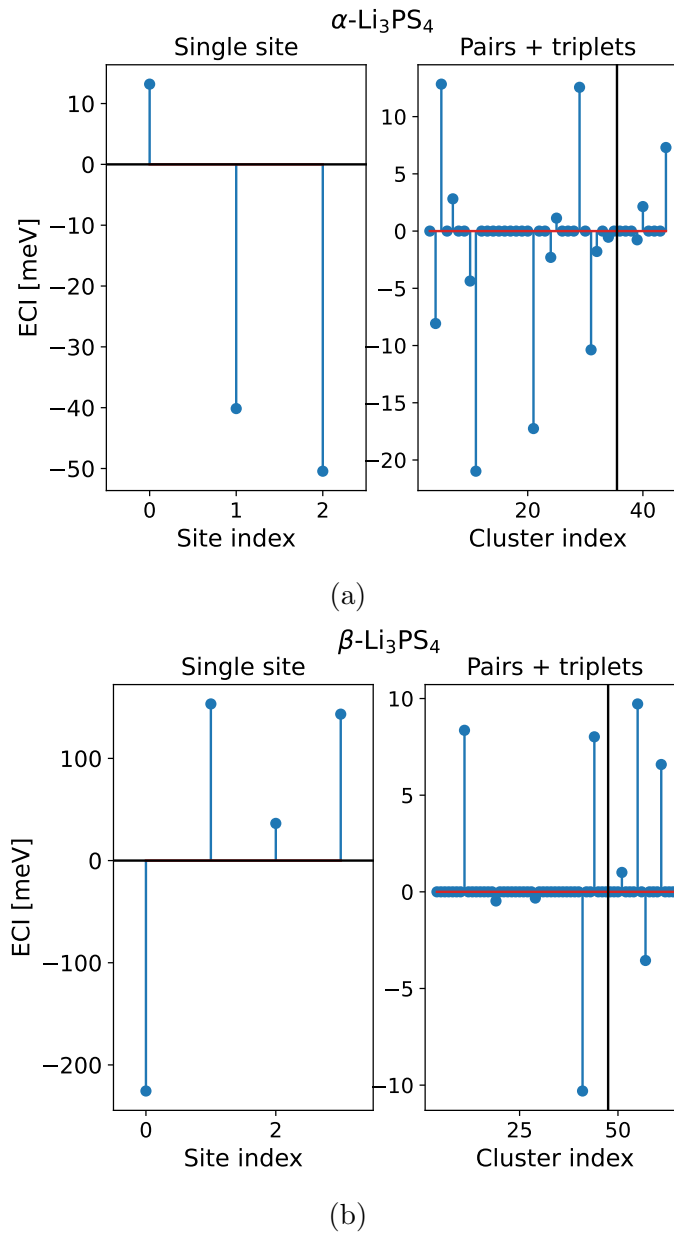


Figure 4.17: CE training and cross-validation errors.

Figure 4.18: ECI of α - and β -Li₃PS₄ CE models.

Chapter 5

Phase Stability and Electronic Structure of the LiMnO_2 Polymorphs

5.1 Introduction

Many conventional Li cathode materials are synthesized with the chemical formula LiMO_2 , where M can be either a single species or an admixture of TMs and other metals. These are rock-salt type structures, in which the oxygen (O) sublattice is face-centered cubic (FCC) and the cations are distributed in the interstitial octahedral sites of the anion sublattice. Commonly used LiMO_2 cathode compositions are typically rich in either Ni or Co, and crystallize in a layered structure with the $R\bar{3}m$ space group [6, 7, 188]. However, extensive use of Ni and Co can potentially lead to future supply chain bottlenecks [4, 5], thus motivating our study of Mn-based cathode materials. LiMnO_2 is particularly unique because its ground state is the orthorhombic (Pmmn) phase [188, 189, 190] – in contrast with the Ni and Co counterparts – and is characterized by corrugated layers of Li and Mn. This type of cation ordering is not observed as the ground state in any other reported LiMO_2 composition [188].

To date, various LiMnO_2 phases have been explored as potential cathode materials. In particular, three LiMnO_2 polymorphs have been experimentally reported: (i) the aforementioned orthorhombic (Pmmn), (ii) the (lithiated) spinel ($I4/amd$), and (iii) the layered ($C2/m$) phases; these are shown in Figures 5.1a-c, respectively [190, 191, 192, 193]. In these LiMnO_2 phases, a Jahn-Teller (JT) distortion of Mn^{3+} occurs, characterized by the elongation of two axial Mn-O bonds and the shortening of four equatorial Mn-O bonds within the MnO_6 octahedra [194]. The direction of the (longer) axial Mn-O bonds, which we will refer to as the JT axis, are highlighted in orange in Figure 5.1. The JT axes within the experimentally refined orthorhombic (ortho), spinel, and layered LiMnO_2 phases are collinearly aligned (Figures 5.1a-c) [195, 196, 197, 191, 192, 193]. The collinear ordering of JT distortions leads to a lowering of symmetry in layered LiMnO_2 ($C2/m$ space group) compared to layered LiNiO_2 and LiCoO_2 ($R\bar{3}m$ space group) [188, 6, 7]. The tetragonal symmetry of

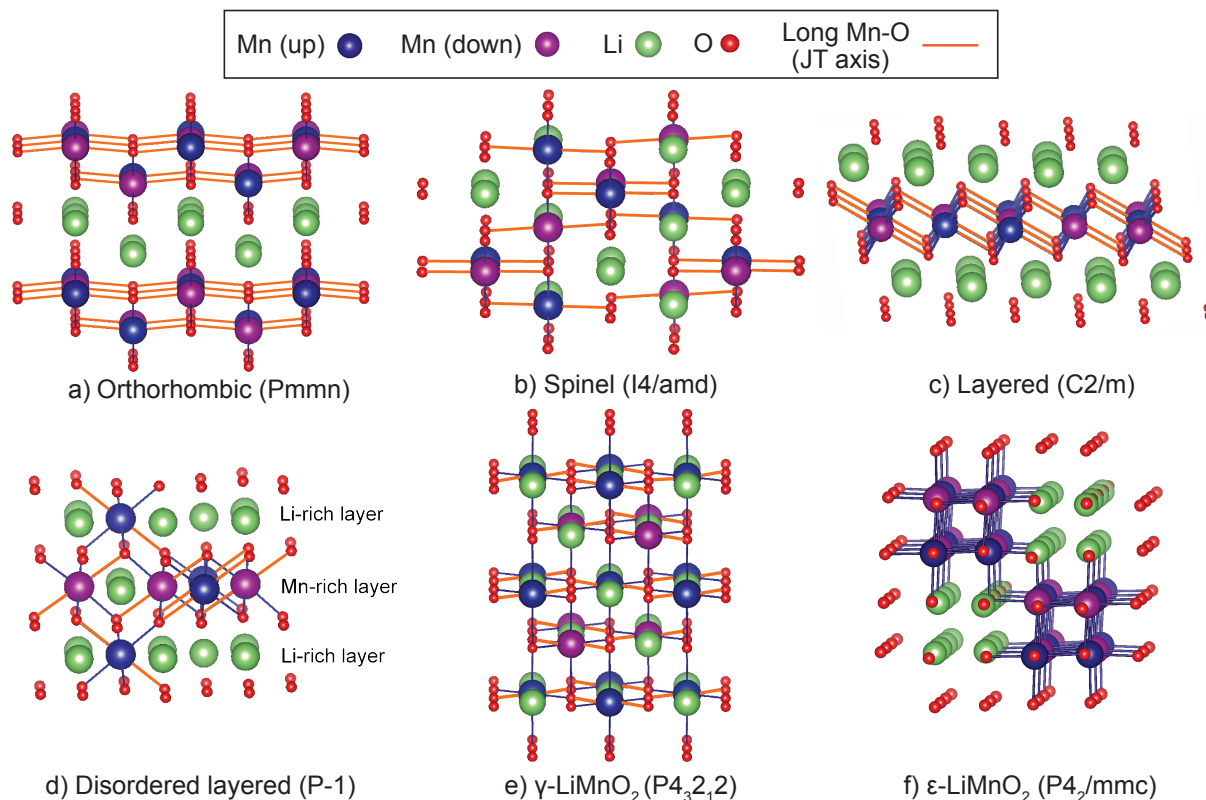


Figure 5.1: Structures of the LiMnO_2 phases that are examined in this study. The majority (up, purple) and minority (down, blue) spin channels of Mn are distinguished to display the ground state AFM orderings that we identify. The long Mn-O bonds (JT axis) are shown in orange and Li-O bonds are omitted for clarity. The space groups are labeled in parentheses. The spinel phase (b) is specifically the lithiated spinel ($\text{Li}_2\text{Mn}_2\text{O}_4$ in spinel notation). In $\epsilon\text{-LiMnO}_2$ (f), all JT axes are aligned perpendicular to the page and are not visible in the figure.

spinel LiMnO_2 (or $\text{Li}_2\text{Mn}_2\text{O}_4$ in spinel notation) also arises from the collinear ordering of JT distortions, as the delithiated states of spinel LiMn_2O_4 and $\lambda\text{-MnO}_2$, which contain some or all Mn^{4+} , have cubic symmetry ($\text{Fd}\bar{3}\text{m}$) at ambient temperature [193, 198].

Previous experiments have indicated that these LiMnO_2 phases are thermodynamically competitive with each other. The ortho phase is experimentally known to be the ground state [195, 190], but differences in the synthesis precursors or conditions can lead to layered or spinel forming as impurity phases [199, 200, 201]. The substitution of some Mn by Al or many other metals can lead to increased stability of the layered phase [202, 189]. Phase-pure layered LiMnO_2 can be synthesized typically through ion-exchange from NaMnO_2 [191, 192]. Phase-pure spinel LiMnO_2 can be formed by lithiating spinel LiMn_2O_4 [203]. When layered

or ortho- LiMnO_2 are electrochemically cycled, they tend to transform to a spinel-like phase [204, 199, 200, 201].

These experimental observations suggest that the free energy differences among these LiMnO_2 phases should be relatively small. Thus, quantifying the relative stability of these polymorphs using *ab initio* calculations would provide valuable insights, and is the objective of our investigation. As we will show, capturing the relative energy differences among LiMnO_2 polymorphs is complicated by the strong interplay between electron localization, JT distortions, and magnetic ordering, making this a challenging test case for modern electronic structure theory. In an early study, Mishra et al. showed that capturing antiferromagnetic (AFM) order and use of accurate density-functional theory (DFT) techniques are required to predict ortho as the lowest energy structure among the experimentally known LiMnO_2 phases [189]. In our study we apply a similar analysis, but using more recently developed DFT methodologies. We further investigate additional LiMnO_2 orderings that have not been experimentally reported and previously overlooked in *ab initio* studies, but that we find to have comparable energies to the known phases. These phases are: i) the disordered layered phase, which is a layered structure containing 25% mixing between Li and Mn layers, ii) γ - LiMnO_2 , which has the same cation order as the γ - LiFeO_2 phase [205], and iii) ϵ - LiMnO_2 where Mn and Li are ordered into nearest cation neighbor Mn_4 and Li_4 tetrahedral columns. The ϵ phase is a low-energy structure that we have found from Monte Carlo simulations performed using a cluster expansion lattice model trained on the rock-salt LiMnO_2 - Li_2MnO_3 phase space. The disordered layered, γ , and ϵ - LiMnO_2 phases are shown in Figure 5.1d-f, respectively. We note that the (DFT-relaxed) structures of disordered layered (Figure 5.1d) and γ (Figure 5.1e) contain JT axes that are not all collinearly aligned, which is different from ortho, layered, spinel, and ϵ (Figures 5.1a,b,c,f).

In order to accurately model these LiMnO_2 phases, *ab initio* methodologies that can precisely capture the localized nature of Mn-3d states are needed, which presents a challenge for DFT approximations [105, 121]. Specifically, the self-interaction error (SIE) [88] that is inherent to semi-local DFT approximations tends to be especially large in localized 3d states, and it can contribute to the over-delocalization of 3d electrons, incorrect prediction of metallic states in insulating TM oxides [121, 106], and poor prediction of TM oxidation reaction energies [123], as extensively discussed in Chapter 3.1. To overcome these limitations, Hubbard corrections are conventionally added to generalized gradient approximation (GGA) functionals, within the so-called GGA+ U (+ V) approach [123, 122, 125, 129], where U and V are on-site and inter-site Hubbard parameters (HP), respectively. These HPs can be determined from empirical fitting [123] or first-principles linear response DFT calculations [122]. An alternative strategy to mitigate the SIE in GGA involves incorporating a fraction of exact (Fock) exchange into the electronic exchange energy calculation, as implemented in hybrid functional methods [108]. Hybrid-GGA functionals, particularly HSE06 [109], have been demonstrated to accurately predict lattice parameters, formation energies, and band gaps of TM oxides [110, 113, 111].

Another way of building upon the GGA functional is to incorporate electron kinetic-energy density corrections to the exchange-correlation energies, in the so-called meta-GGA functionals. Meta-GGAs, particularly the SCAN family (SCAN, rSCAN, r²SCAN), have consistently outperformed GGAs in predicting formation enthalpies and structural properties [96, 97, 206, 101, 102, 99, 98]. Kitchaev et al. further demonstrated SCAN’s superior accuracy in modeling the MnO_2 polymorph energetics within TM oxides [100]. Refer to Chapter 3.1 for a more extensive description of the various DFT approximations.

In this work, we apply the DFT methods we discussed above, namely $\text{GGA}+U(+V)$, $\text{r}^2\text{SCAN}(+U)$, and HSE06 to evaluate the phase stability of the LiMnO_2 polymorphs. The paper is organized as follows: in Section 5.2, we provide the details of the computational schemes we used, while in Section 5.3, the LiMnO_2 phase stability results are presented. We find that accounting for AFM order is vital to obtain more accurate phase stability trends across several levels of theory, which is consistent with the results of Mishra et al. [189] and Singh [207]. We encounter challenges when applying PBEsol [95] and r^2SCAN [101] with or without empirically tuned values of Hubbard U , to the various AFM LiMnO_2 phases, as the predicted ground state is the γ - LiMnO_2 phase and not the orthorhombic LiMnO_2 , which is inconsistent with experimental observations. We are thus required to assess more computationally complex schemes such as HSE06 and PBEsol with self-consistent Hubbard parameters. Using these computational methodologies, we recover relative energies in closer agreement with experiments. We assess the phase stability at elevated temperature by performing harmonic phonon calculations within $\text{PBEsol} + U$ and determine the vibrational free energy as a function of temperature. To rationalize the differences in predicted phase stability, we analyze the properties related to the electronic structure that each method yields. Specifically, in Section 5.4, the self-consistently calculated HP in all LiMnO_2 phases and their correlation with the structural and electronic properties are examined. In Section 5.5, we analyze electronic properties such as the electron density, density of states, and band structure of ortho- LiMnO_2 across the different DFT approximations. In the absence of experimental data on the electronic structure, we present theoretical predictions of the band structure and excitation energies. Our calculations using HSE06 and GW characterize the system as a wide band gap insulator, with the band gap estimated to be > 3 eV. In the Discussion (Section 5.6), we further rationalize the relation between the ion configuration, electronic structure, and phase stability trends in these polymorphs.

5.2 Methods

We use a variety of DFT functionals to perform structural relaxations and calculate total energies of the LiMnO_2 phases. The Vienna *ab initio* Simulation Package (VASP) [70, 183, 80] is used for the structural relaxations performed within $\text{PBEsol} + U$, $\text{r}^2\text{SCAN}(+U)$, and HSE06. When “ $+U$ ” is used, a Hubbard U is applied on the Mn-3d manifolds with values of U that have been empirically fitted in previous studies [123, 104]. The `pymatgen` package is

used to generate and manipulate structures, create calculation inputs, parse the calculation outputs [50], identify symmetries, and compute X-ray diffraction (XRD) patterns. **Quantum ESPRESSO (QE)** [69] is used for its implementation of extended Hubbard parameters (PBEsol+ $U+V$) and density functional perturbation theory (DFPT) for self-consistent calculations of Hubbard U and V parameters [129, 128, 208]. The details of the DFT calculations, including the pseudopotentials, energy cutoff, and convergence criteria are listed in Appendix (Chapter 5.9). To demonstrate the consistency between the energy differences obtained with VASP and QE, we use them to evaluate the energies of the LiMnO_2 phases using PBEsol+ U , scanning U from 3 to 7 eV. The results are reported in Appendix Figure 5.13, which show good compatibility between the two codes. The ϵ phase was found from canonical Monte Carlo (MC) simulations at the LiMnO_2 composition, using a cluster expansion (CE) on a rock-salt $\text{Li}^+-\text{Mn}^{3+}-\text{Mn}^{4+}-\text{O}^{2-}$ lattice.

The AFM ground state of each phase is identified by enumerating ~ 30 collinear AFM orderings and relaxing each structure within PBEsol+ U ($U = 3.9$ eV, VASP). The AFM orderings were enumerated using the **MagneticStructureEnumerator** module developed by Horton et al. in **pymatgen** [209, 50]. The AFM ground state of ortho- LiMnO_2 that we identify is identical to the AFM structure that was experimentally refined by Greedan et al. using neutron diffraction (ND) [195].

The self-consistent calculations of the Hubbard parameters (HP) within PBEsol are performed using DFPT as implemented in the HP module of QE [128]. To converge the HP, we perform iterations in which U and V are computed using DFPT followed by a relaxation of the structure with these HP within PBEsol+ $U+V$. This procedure is repeated until all U and V values are converged to within 10 meV between iterations. The values of the converged HP are shown and analyzed in Section 5.4. Each DFPT calculation requires the ground state electron density and wavefunctions, which are computed from static self-consistent field (SCF) calculations within PBEsol+ $U+V$. We also compute the self-consistent Hubbard U within r²SCAN using QE, using the finite-difference linear response approach based on supercells [122] instead of DFPT, since the current version of QE (version 7.4) does not support DFPT calculations with meta-GGA functionals. The r²SCAN calculations in QE are performed using the interface with the Libxc library of density functionals [210]. Furthermore, we perform the self-consistent calculation of U for r²SCAN at the structural geometries relaxed using VASP, since variable-cell structural optimizations are not yet implemented for r²SCAN in QE. Due to the current limitations of the codes, we present the r²SCAN+ U_{sc} results in the Appendix. More details of the self-consistent HP calculations are shown in the Appendix (Chapter 5.9).

To obtain the vibrational properties, harmonic phonon calculations are computed using the frozen phonon method with Phonopy and VASP [59]. Each LiMnO_2 phase is relaxed within its respective AFM ground state and atomic displacements are generated on a supercell. The dynamical matrix is constructed by computing the forces in each supercell by

performing SCF calculations. We use PBEsol + U ($U = 3.9$ eV) for the phonon calculations, as it has been previously shown that PBEsol + U can predict phonon frequencies with good accuracy in a range of TM oxides [211, 212, 213, 94].

In Section 5.5, we compute the electronic structure of ortho-LiMnO₂ using the range of DFT functionals we have discussed, to obtain the electron density, density of states, magnetic moments, and band gaps. For these calculations, we fix the atomic positions to the primitive cell of the AFM ortho-LiMnO₂ structure that was previously refined from ND by Greedan et al. [195]. The band structure of ortho-LiMnO₂ is computed using PBEsol + U , HSE06, and one-shot GW . SeeK-path is used to select the high symmetry path through the first Brillouin zone [214], which satisfies the magnetic symmetry of the primitive cell of AFM ortho-LiMnO₂ described by the C2/c space group, which is of lower symmetry than the non-magnetic structure (Pmmn). The PBEsol + U band structure is computed using QE and its ground state wave functions are used as a starting point for the GW calculations, which are performed using BerkeleyGW [144, 145]. The single-particle Green's function (G) and screened Coulomb interaction (W) are constructed using the wave functions generated from PBEsol + U . To calculate W , the dielectric matrix (ϵ) is computed within the random phase approximation. More details are shown in the Appendix (Chapter 5.9).

5.3 Phase stability

We evaluate the phase stability of the LiMnO₂ polymorphs at 0 K by performing structural relaxations and calculating the total energy using PBEsol + U , r²SCAN, and r²SCAN + U ($U(\text{PBEsol}) = 3.9$ eV [123] and $U(\text{r}^2\text{SCAN}) = 1.8$ eV [104]). Within each functional, we evaluate the energy of each structure relative to ortho-LiMnO₂ with all structures containing either FM or AFM spin ordering, as shown in Figures 5.2a and 5.2b, respectively. Hereafter, we use the notation $\Delta E_X \equiv E_X - E_{\text{ortho}}$ to represent the energy of phase X relative to ortho-LiMnO₂, where a positive value of ΔE_X implies that ortho-LiMnO₂ is lower in energy than X.

The results in Figure 5.2a show that with FM spin order, the ortho phase is higher in energy than *all* the considered LiMnO₂ polymorphs, with the exception of ϵ . The γ -LiMnO₂ structure is clearly the ground state as $\Delta E_\gamma \approx -30$ meV/atom. Disordered layered is the second lowest in energy and is ~ 8 meV/atom below layered LiMnO₂. Layered and spinel are both predicted to be slightly lower in energy than ortho by < 5 meV/atom. The trends produced by all the applied DFT functionals are similar.

These results clearly contradict experimental observations reporting ortho as the ground state [195, 190]. The prediction of γ to be the ground state is almost certainly incorrect, as the γ -LiFeO₂-like cation ordering has never been reported for the LiMnO₂ composition. Furthermore, disordered layered is predicted to be lower in energy than layered, implying a

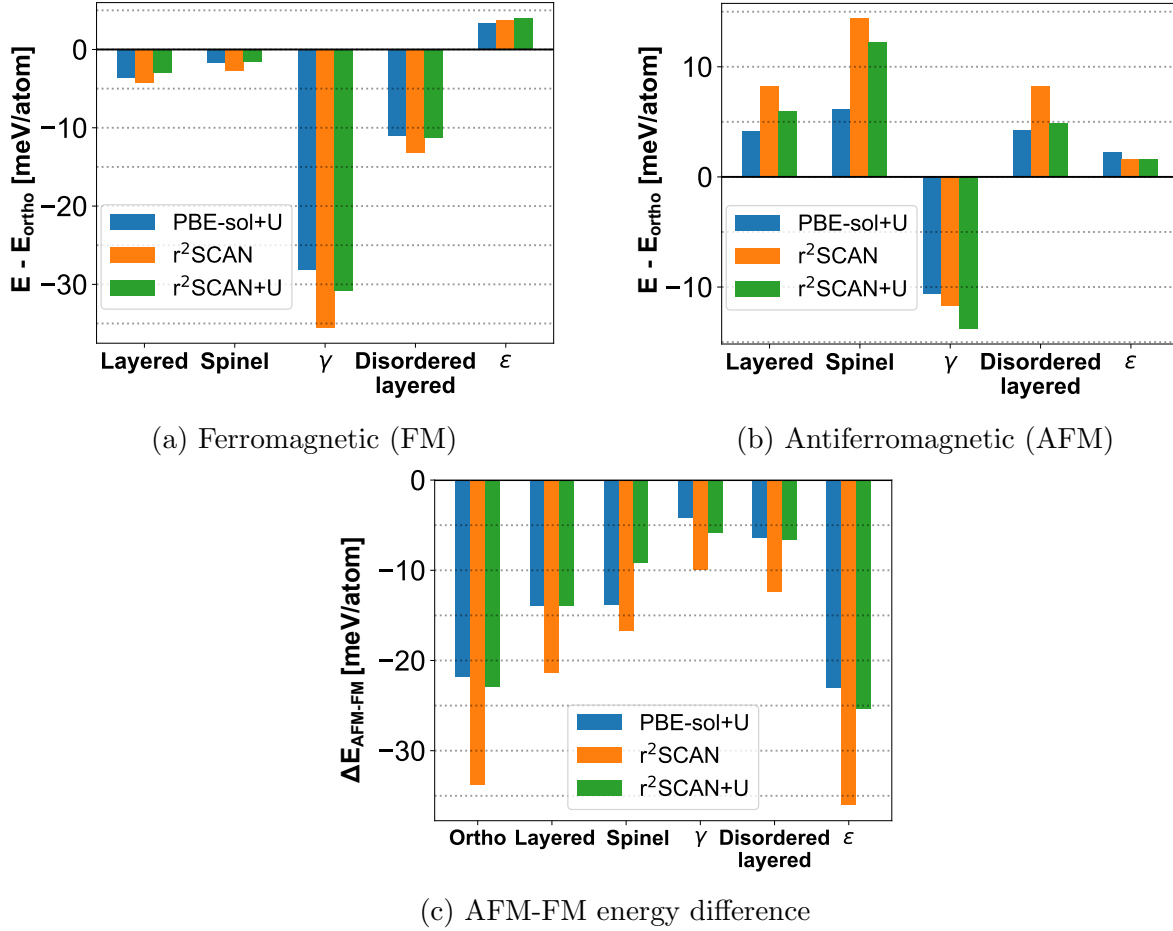


Figure 5.2: DFT energy of LiMnO_2 phases relative to ortho- LiMnO_2 in the a) FM and b) AFM spin configurations, and c) energy differences between the AFM and FM spin orderings ($\Delta E_{\text{AFM-FM}}$). Energies are computed with PBEsol + U ($U = 3.9$ eV), $r^2\text{SCAN}$, and $r^2\text{SCAN}+U$ ($U = 1.8$ eV) in VASP.

negative anti-site defect formation energy, which is inconsistent with the synthesis of well-ordered metastable layered LiMnO_2 [191, 192].

With AFM spin ordering (Figure 5.2b), γ remains the ground state, but its energetic advantage over the orthorhombic structure has decreased compared to the FM case (Figure 5.2a). The ϵ structure is again slightly higher in energy than ortho but more stable than layered and spinel. There is no significant energy difference between disordered layered and layered LiMnO_2 .

The notable differences in phase stability predicted with AFM order compared to the FM case indicate that the influence of magnetic order on the total energy varies greatly by phase,

consistent with earlier findings [189]. To quantify the effect of magnetic configuration, we calculate the energy difference between the AFM and FM configurations ($\Delta E_{\text{AFM-FM}}$) for each LiMnO₂ phase and plot them in Figure 5.2c. We find that all structures are significantly more stable in their AFM ground state compared to the FM state. Ortho and ϵ are stabilized the most by AFM order, with $\Delta E_{\text{AFM-FM}} \approx -20$ to -25 meV/atom (≈ -80 to -100 meV/Mn) within PBEsol + U or r²SCAN + U . While AFM order also lowers the energy of layered and spinel, ($\Delta E_{\text{AFM-FM}} \approx -10$ to -15 meV/atom) its effect is slightly smaller in magnitude than for ortho and ϵ . Within the γ and disordered layered structures, $\Delta E_{\text{AFM-FM}}$ is smaller (~ 5 meV/atom). These variations in $\Delta E_{\text{AFM-FM}}$ explain why the order of phase stability changes when all structures are in their AFM ground state compared to the FM case. We note that the absolute values of $\Delta E_{\text{AFM-FM}}$ calculated from r²SCAN are consistently larger compared to PBEsol + U and r²SCAN + U . Despite this discrepancy, the qualitative trends of $\Delta E_{\text{AFM-FM}}$ among these phases are similar across these DFT approximations.

The phase stability predicted within AFM order are more consistent with experiment than in the FM case, as ortho is lower in energy than layered and spinel (Figure 5.2b). But certain trends are still questionable, as γ is the predicted ground state and ϵ is lower in energy than layered and spinel. Furthermore, the degeneracy of disordered layered and layered would indicate that there is no energy requirement to form specific anti-site defects in layered. We thus assess the phase stability of the LiMnO₂ polymorphs using electronic structure methods that enforce electron localization in more select ways, such as PBEsol + $U + V$ and the HSE06 hybrid functional. We also assess whether employing self-consistently calculated U and V parameters (PBEsol + $(U + V)_{\text{sc}}$) can significantly affect the results. We thus evaluate the energy of each AFM LiMnO₂ phase relative to ortho using HSE06, PBEsol + U_{sc} , and PBEsol + $(U + V)_{\text{sc}}$, with the results shown in Figure 5.3.

Using these DFT functionals, we largely recover the experimental trends across all the investigated LiMnO₂ phases. HSE06 (purple bars in Figure 5.3) correctly predicts the ortho phase to be the ground state of LiMnO₂, although it is only marginally (≈ 1 meV/atom) lower in energy than γ . The ϵ structure is only slightly higher in energy than ortho ($\Delta E_{\epsilon} \approx 2$ meV/atom) and lower in energy than layered and spinel. Disordered layered becomes ~ 7 meV/atom higher in energy than layered, which corresponds to a substantial anti-site defect formation energy ($\Delta E_{\text{a-s,f}}$) of 112 meV/defect (there is one defect per Li₄Mn₄O₈ in disordered layered).

The phase stability predicted within PBEsol + $(U + V)_{\text{sc}}$ (green bars in Figure 5.3) shares similar features with HSE06. Ortho is predicted to be the ground state. However, γ and disordered layered are both significantly higher in energy relative to ortho ($\Delta E_{\gamma} \approx \Delta E_{\text{dis lay}} \approx 25$ meV/atom). This energy difference corresponds to $\Delta E_{\text{a-s,f}} \approx 400$ meV/defect in layered, which is much larger than the value predicted by HSE06. The energy of layered, spinel, and ϵ relative to ortho-LiMnO₂ are in close agreement with HSE06. If we neglect the intersite V parameter and include only the self-consistent on-site U correction (PBEsol + U_{sc}

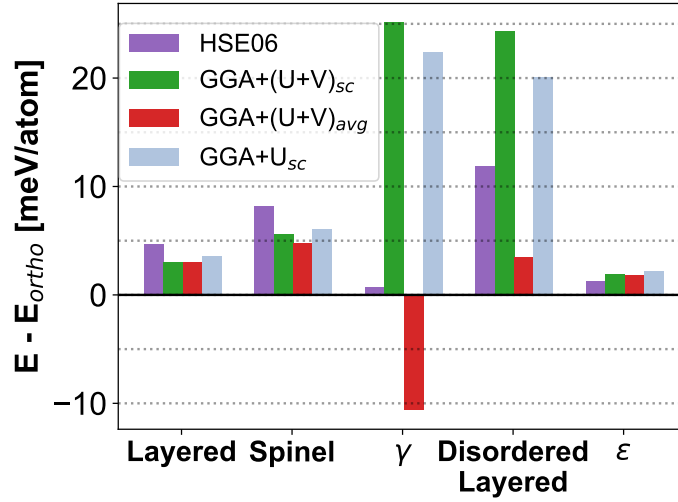


Figure 5.3: DFT energy of the LiMnO_2 polymorphs relative to ortho, in their respective ground state AFM spin configurations. The functionals used are HSE06, PBEsol (GGA) with self-consistently (sc) determined U (PBEsol+ U_{sc}), PBEsol+($U + V$)_{sc}, and PBEsol with averaged (avg) $U = 6$ eV and $V = 0.6$ eV.

– light blue bars in Figure 5.3), we find that the energy differences are very close to the PBEsol + ($U + V$)_{sc} results. The only significant differences are that ΔE_γ and $\Delta E_{\text{dis lay}}$ are slightly smaller in PBEsol + U_{sc} compared to PBEsol + ($U + V$)_{sc}. Thus, capturing the variations in self-consistent U gives the leading contribution for an accurate prediction of LiMnO_2 phase stability.

We note that we have evaluated the LiMnO_2 energetics using $\text{r}^2\text{SCAN} + U_{\text{sc}}$, as shown in Appendix Figure 5.15, which largely recovers the same trends as PBEsol + U_{sc} (+ V_{sc}) – namely ortho is the ground state, γ is significantly higher in energy than ortho, and disordered layered is higher in energy than layered. There are discrepancies in our linear response calculations of U within r^2SCAN compared to PBEsol, primarily since DFPT and variable-cell structural relaxations within r^2SCAN are not yet implemented in the current version of QE; for this reason these results are reported in the Appendix (Chapter 5.9).

The LiMnO_2 energies are also evaluated using PBEsol with averaged Hubbard parameters (PBEsol + ($U + V$)_{avg}) of $U = 6$ eV and $V = 0.6$ eV, which are roughly the average of the self-consistent U and V values across all the structures (red bars in Figure 5.3). PBEsol + ($U + V$)_{avg} yields the spurious phase stability trends that were observed in PBEsol + U and $\text{r}^2\text{SCAN}(+U)$ (Figure 5.2b) – namely, γ is the predicted ground state and disordered layered is nearly equal in energy to layered. Therefore, the self-consistently calculated and structurally-informed Hubbard parameters are essential in order to obtain relative phase stability that is more consistent with experiments.

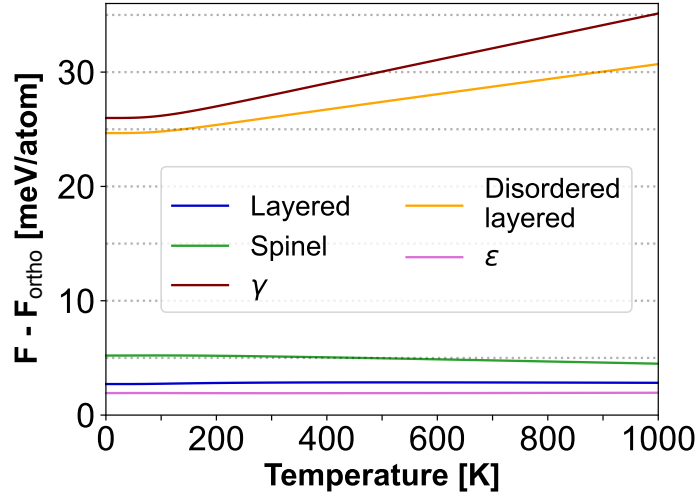


Figure 5.4: Total free energy (F) relative to ortho- LiMnO_2 as a function of temperature. $F(T)$ is the sum of the vibrational free energy and DFT energy. Harmonic phonon calculations are performed within PBEsol + U ($U = 3.9$ eV) and DFT energies are computed within PBEsol + $(U + V)_{\text{sc}}$.

The phase stability assessed thus far has been restricted to $T = 0$ K. We include finite-temperature effects by evaluating the harmonic phonon contribution to the free energy ($F_{\text{vib}}(T) = E_{\text{vib}}(T) - TS_{\text{vib}}(T)$) and adding it to the electronic PBEsol+ $(U + V)_{\text{sc}}$ total energy at 0 K (E_{ele}): $F(T) = E_{\text{ele}}(T = 0) + F_{\text{vib}}(T)$. For simplicity, we evaluate $F_{\text{vib}}(T)$ only at the PBEsol + U level in the AFM configuration. Figure 5.4 shows the calculated $F(T)$ of each phase relative to ortho- LiMnO_2 as a function of temperature from 0 to 1000 K (we denote $\Delta F_x(T)$ as the free energy difference of phase X relative to ortho). The free energy of ortho is lower than all the other phases across the entire temperature range considered. The experimentally observed metastable layered and spinel are only < 5 meV/atom higher in energy than ortho- LiMnO_2 across this temperature range. The ϵ phase is ≈ 2 meV/atom higher in energy than ortho and slightly lower in energy than both layered and spinel. The changes in $\Delta F_x(T)$ for layered, spinel, and ϵ are small (< 1 meV/atom) across this temperature range. For the γ and disordered layered phases, $\Delta F_x(T)$ increases significantly with temperature. Thus, the vibrational entropy appears to help stabilize ortho, layered, spinel, and ϵ relative to the γ and disordered layered phases at elevated temperature.

5.4 Self-consistent Hubbard parameters

We have shown that the phase stability predicted with HSE06, PBEsol + $U_{\text{sc}}(+V_{\text{sc}})$, and $\text{r}^2\text{SCAN} + U_{\text{sc}}$ better reflects experimental observations, compared to those obtained with PBEsol and r^2SCAN , with or without empirical Hubbard parameters (HPs). Specifically,

Table 5.1: Hubbard on-site U (Mn-3d), inter-site V (Mn3d – O 2p) parameters, and JT bond ratios ($\frac{\text{avg. long}}{\text{avg. short}}$) in the LiMnO₂ phases. Hubbard parameters (in units of eV) are self-consistently calculated using DFPT. Only the distinct values of each property are listed. V of the short (1.9-2.0 Å) and long (2.2-2.3 Å) Mn-O bonds are shown in separate rows. Reference values of the JT bond ratios from experimentally refined structures are listed.

Method	Property	Orthorhombic	Layered	Spinel	γ	Disordered layered	ϵ
PBEsol	U	5.81	5.79	5.81	6.36	5.92, 6.25, 6.34	5.81
+ $U + V$	V (short)	0.72, 0.59	0.65	0.66, 0.65	0.74 - 0.79	0.64 - 0.77	0.71, 0.59
	V (long)	0.38	0.30	0.31	0.57, 0.54	0.36 - 0.57	0.35
	JT bond ratio	1.189	1.203	1.200	1.152	1.156, 1.211, 1.138	1.190
PBEsol	U	6.01	6.01	6.02	6.49	6.08, 6.40, 6.44	6.01
+ U	JT bond ratio	1.181	1.191	1.189	1.134	1.148, 1.189, 1.125	1.181
Exp	JT bond ratio	1.182, 1.192 [195, 196] 1.194 [197]	1.201 [191]	–	–	–	–

all the methods with empirical or averaged HPs, whether with an on-site U or including inter-site V , yield the γ phase to be the ground state. We believe this result to be almost certainly incorrect since γ has never been experimentally reported for LiMnO₂.

The self-consistently determined Hubbard parameters from the PBEsol + $(U + V)_{\text{sc}}$ and PBEsol + U_{sc} calculations of each phase are listed in Table 5.1. Importantly, as shown by Timrov et al., these computed HPs are not transferable across different pseudopotentials or forms of Hubbard projectors, since they can have different degrees of localization [128, 129]. Within PBEsol + $(U + V)_{\text{sc}}$, the self-consistent U of γ -LiMnO₂ is 6.4 eV, which is ~ 0.6 eV larger than that in ortho, layered, spinel, and ϵ -LiMnO₂ ($U \sim 5.8$ eV). In the disordered layered phase, the calculated U span a range of values (5.92 – 6.34 eV). Within PBEsol + U_{sc} , the trends among the calculated Hubbard U are qualitatively similar, with the key difference being that the Hubbard U parameters of each phase are systematically larger by ~ 0.17 eV on average compared to PBEsol + $(U + V)_{\text{sc}}$. Within r²SCAN, the values of U are ~ 4.5 eV (Appendix Table 5.6), which are systematically smaller by > 1 eV compared to PBEsol; though we note that the differences between the Hubbard U calculated within r²SCAN and PBEsol arise in part due to the different pseudopotentials used (more details in the Appendix). The larger values of the calculated Hubbard U in γ and disordered layered are very likely the main reason why these phases are predicted to be unstable relative to ortho-LiMnO₂ within PBEsol + U_{sc} (+ V_{sc}) and r²SCAN + U_{sc} . Therefore, the phase stability trends can be dictated by the nature of electron-electron interactions, which are more genuinely captured by the HPs calculated from the linear response framework.

We also observe variations in the extent of Mn JT distortions in each phase, which we measure by evaluating the ratio between the averaged long Mn-O bond length and averaged short Mn-O bond length (we will refer to this quantity as the JT bond ratio = $\frac{\text{avg. long}}{\text{avg. short}}$).

Within $\text{PBEsol} + (U + V)_{\text{sc}}$, the predicted JT bond ratio of γ is significantly smaller than that of ortho, layered, spinel, and ϵ (Table 5.1). Within disordered layered, the JT bond ratios, as well as the Hubbard U , span a range of small and large values. These trends are also observed within $\text{PBEsol} + U_{\text{sc}}$, which suggests that the self-consistent U and extent of JT distortion are related. The predicted JT bond ratios within $\text{PBEsol} + U_{\text{sc}}$ are systematically smaller compared to $\text{PBEsol} + (U + V)_{\text{sc}}$, which we attribute to the increased electron localization when excluding the inter-site V term. In general, the JT bond ratios predicted by $\text{PBEsol} + (U + V)_{\text{sc}}$ are in better agreement with the experimentally refined structures of orthorhombic and layered LiMnO_2 in the International Crystal Structure Database (ICSD), although the differences between $\text{PBEsol} + (U + V)_{\text{sc}}$ and $\text{PBEsol} + U_{\text{sc}}$ are rather small.

The variations in the Hubbard parameters can also be correlated with the local electronic structure and bonding environments. We provide correlation plots between the self-consistent values of U (from $\text{PBEsol} + (U + V)_{\text{sc}}$) and Mn magnetic moments in Figure 5.5a, and the values of V with Mn-O bond length in Figure 5.5b. There is a strongly linear relation between Hubbard U and Mn magnetic moment, with a coefficient of determination $R^2 = 93.96\%$ (Figure 5.5a). A similar linear relation is also found for $\text{PBEsol} + U_{\text{sc}}$ (shown in Appendix Figure 5.14). This strongly linear relation between U and Mn moment indicates that the self-consistent U reflects the degree of electron localization on each Mn site. To demonstrate that the variation in Mn magnetic moments is not an artifact of the distinct values of applied HPs, we compare the Mn magnetic moments calculated using averaged HPs ($U = 6$ eV and $V = 0.6$ eV) with the Mn moments calculated using $\text{PBEsol} + (U + V)_{\text{sc}}$ in Appendix Figure 5.17, which shows that the magnetic moments from both methods are very close (RMSE = $0.008 \mu_{\text{B}}$).

The larger values of U specifically arise on Mn atoms that are part of 180° Mn-O-Mn complexes in which one Mn-O bond is long (~ 2.3 Å) and the other is short (~ 1.9 Å). In the following discussion, we will refer to a Mn taking part in this type of complex as possessing a “noncollinear” JT distortion, while the Mn that do not as having a “collinear” JT distortion. In Figure 5.5a, we see that the Mn atoms with collinear JT (green squares) have significantly smaller values of Hubbard U and magnetic moment ($\text{PBEsol} + (U + V)_{\text{sc}}$) compared to the Mn with noncollinear JT (orange crosses). In ortho, layered, spinel, and ϵ - LiMnO_2 , the JT axes are all collinearly ordered (structures shown in Figure 5.1), which leads to a smaller U compared to γ - LiMnO_2 , in which the Mn have a noncollinear JT distortion and larger U . Given that the elongated Mn-O JT axis reflects a filled e_g orbital, the non-collinear arrangement almost certainly reflects filled-empty orbital ordering, consistent with the higher degree of localization and higher U value.

In the disordered layered phase, the mixing between Mn and Li layers leads to distinct Mn environments that include both collinear and noncollinear JT distortions in the DFT-relaxed configuration. We display the ionic and magnetic structure of disordered layered LiMnO_2 in Figure 5.6, and tabulate the values of Hubbard U and magnetic moment (within

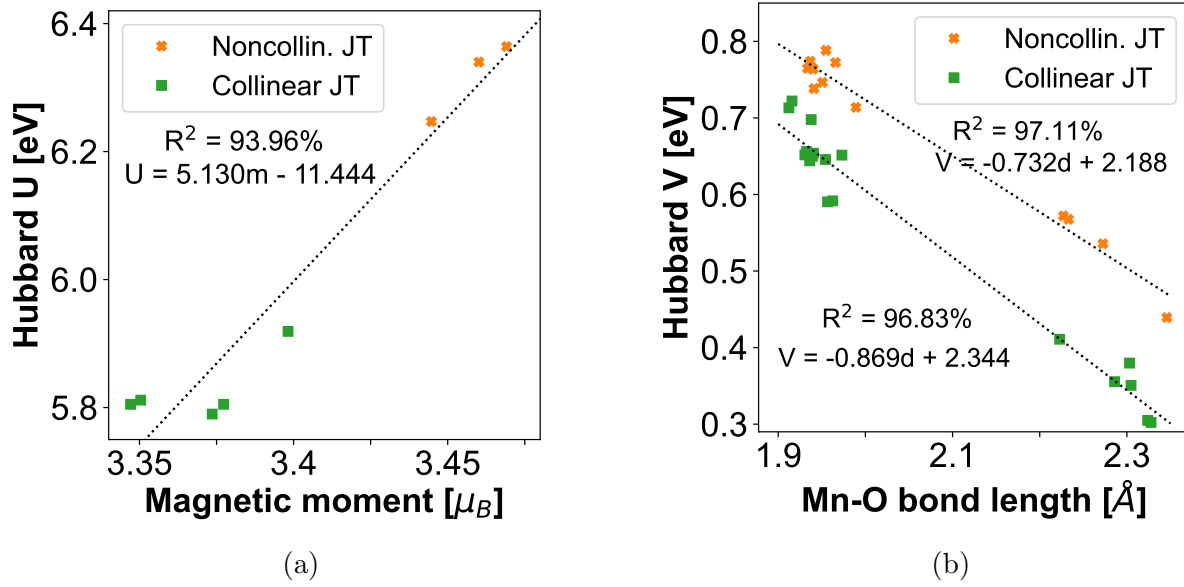


Figure 5.5: Correlating self-consistent HPs from PBEsol + $(U + V)_{\text{sc}}$ with the local electronic structure and bonding environments. Plots of a) Hubbard U with Mn magnetic moment and b) V with Mn-O bond length. All magnetic moments and bond lengths are calculated from the self-consistent HPs. The values of HPs are distinguished by the noncollinear (orange crosses) and collinear (green squares) JT distortions. Lines of best fit and R^2 values are shown.

PBEsol + $(U + V)_{\text{sc}}$ for each distinct Mn site. Mn1 and Mn2 only form 180° Mn-O-Li interactions, and thus we can classify these sites as having collinear JT distortions (Figure 5.6). Consequently, Mn1 and Mn2 have relatively small values of U and absolute value of the magnetic moment. Mn3 and Mn4 take part in 180° Mn-O-Mn interactions with each other, in which one Mn-O bond is long and the other short - thus both have a noncollinear JT distortion. The values of U on Mn3 and Mn4 are significantly greater than that of Mn1 and Mn2.

We also observe a strongly linear correlation between V and the Mn-O bond length ($d_{\text{Mn-O}}$) (Figure 5.5b). On first glance, there appears to be a large spread in the values of V , although the trend of V with $d_{\text{Mn-O}}$ is approximately linear with a R^2 of 80%. The values of V can be partitioned into two groups: one with Mn sites that have a noncollinear JT (orange crosses in Figure 5.5b) and the other group consisting of Mn with collinear JT distortions (green squares in Figure 5.5b). Within these groups, the linear fits of V as a function of $d_{\text{Mn-O}}$ become remarkably more accurate, with $R^2 = 97\%$. The values of V associated with Mn sites that have a collinear JT are significantly smaller than the V on Mn sites with noncollinear JT, as the lines of best fit are separated by > 0.1 eV in the examined range of $d_{\text{Mn-O}}$. Thus the values of Hubbard U and V appear to be correlated to the local Mn-3d

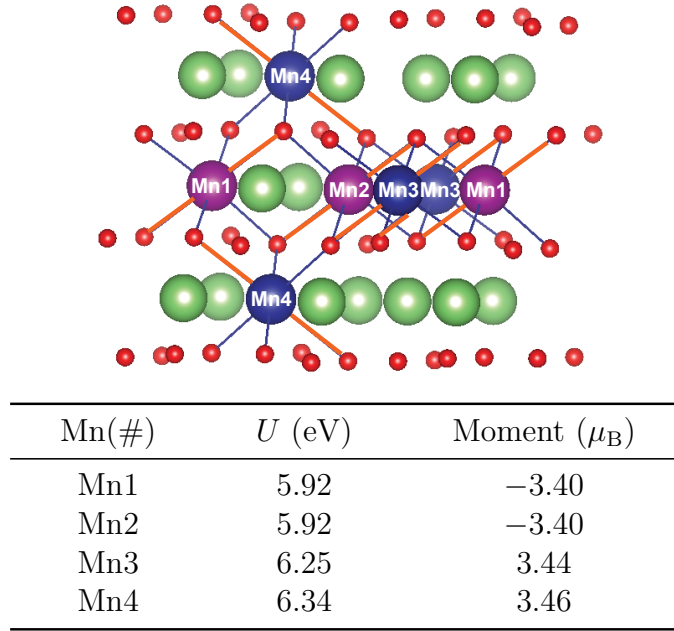


Figure 5.6: Structure of the disordered layered phase and table of Hubbard U and magnetic moments corresponding to each labeled Mn, calculated within PBEsol + $(U + V)_{sc}$. Mn atoms are distinguished by their spins (blue for up-spin, and purple for down-spin). Green atoms - Li, red atoms - O.

orbital ordering. The linear trend between V and $d_{\text{Mn-O}}$ can be rationalized as a shorter bond length reflecting stronger binding between the Mn-3d and O-2p states, and thus leading to a larger hybridizing V value.

5.5 Electronic structure

We have observed large differences in the LiMnO₂ phase stability trends when different magnetic order and DFT approximations are applied. To rationalize these differences, we analyze the electronic structure of ortho-LiMnO₂. For these calculations, we fix the atomic coordinates to the primitive cell of the neutron diffraction refined AFM superstructure [195]. In the following discussion, the HPs imposed on PBEsol are self-consistently calculated at the experimental configuration (shown in Appendix Table 5.7), which are in good agreement with the values shown in Table 5.1.

The electron charge density (ρ) of ortho-LiMnO₂ is computed in the AFM and FM states using PBEsol + $U + V$. The magnetic moment and band gap of these calculations are listed in Table 5.2. We compute the difference in ρ between these two calculations ($\rho_{\text{AFM}} - \rho_{\text{FM}}$) and plot the isosurfaces in Figure 5.7a). In the AFM state, ρ increases predominantly along

Table 5.2: Magnetic moment of Mn and band gap of ortho-LiMnO₂ computed from self-consistent field calculations using various DFT functionals (Quantum ESPRESSO). AFM order is used, unless otherwise stated.

Property	PBEsol	PBEsol + U	PBEsol + $U+V$	PBEsol + $U+V$ (FM)	PBEsol + $U_{\text{Mn,O}}+V$	HSE06
Mn moment [μ_B]	3.00	3.38	3.32	3.35	3.43	3.26
Band gap [eV]	0.9	1.6	2.0	1.2	2.5	3.1

lobes oriented towards the Mn JT axis in the $\hat{c}$ direction (yellow in Figure 5.7), resembling e_g orbitals. The electron density also decreases (blue in Figure 5.7) around Mn along the lobes that are approximately orthogonal to the JT axes, which correspond to t_{2g} -like states. Thus, there appears to be a rearrangement of ρ near Mn, such that electrons are removed from t_{2g} orbitals and fill the e_g orbitals. The shape of the positive isosurface along the e_g states is more diffuse compared to the more localized t_{2g} orbitals, indicating a more pronounced covalency between Mn and the neighboring O along the JT axis. This increased covalency is reflected in the slightly lower Mn magnetic moment in the AFM state (3.32 μ_B) compared to the FM case (3.35 μ_B) (Table 5.2). We also observe significant rearrangement of ρ near each O site, as ρ is decreased from lobes that are oriented along $\hat{c}$ having a $2p$ -orbital shape, and ρ is increased along the $2p$ -like lobes oriented along [110]. The AFM order also leads to a significantly larger band gap compared to FM (2.0 and 1.2 eV, listed in Table 5.2). These substantial changes in electronic structure driven by altering the magnetic order should contribute to the large energy differences calculated using different spin configurations.

To understand the differences between the DFT methods considered, we perform SCF calculations of AFM ortho-LiMnO₂ using PBEsol, PBEsol + U , PBEsol + $U + V$, PBEsol + $U_{\text{Mn,O}} + V$ and HSE06, where $U_{\text{Mn,O}}$ refers to a Hubbard U imposed on both the Mn-3d and O-2p manifolds. The Mn magnetic moment and band gap calculated using each method are presented in Table 5.2. The band gaps increase from PBEsol to PBEsol+ U , to PBEsol + $U + V$, to PBEsol + $U_{\text{Mn,O}} + V$. The magnetic moments do not increase in the same order, as V tends to penalize larger on-site moments. However, all the magnetic moments lie within a reasonable range of each other, from 3 μ_B with PBEsol to 3.43 μ_B with PBEsol + $U_{\text{Mn,O}} + V$.

The energy levels and orbital character of the electronic states can provide insights about the degree of electronic hybridization and localization. The projected density of states (pDOS) from the scf calculations on ortho-LiMnO₂ are shown in Figure 5.8. We examine the energy range from 0 to -8 eV relative to the Fermi level (E_F - which we refer to as the highest occupied energy level) and contains the band manifolds that are mostly Mn-3d and O-2p in character.

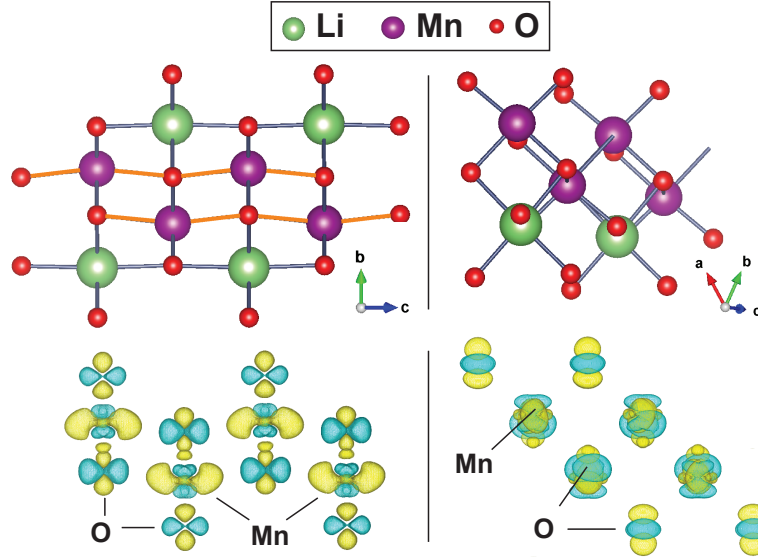


Figure 5.7: Isosurfaces of the difference in charge density (ρ) between FM and AFM states of ortho- LiMnO_2 ($\rho(\text{AFM}) - \rho(\text{FM})$) computed within PBEsol + U + V , visualized at two different crystal orientations as shown in the top panels. The yellow (blue) regions indicate areas of increased (decreased) ρ in the AFM structure. The bonds highlighted in orange correspond to the long bond (~ 2.3 Å) in the Jahn-Teller complex.

In the calculation using PBEsol, the states in the region between 0 to -2 eV are predominantly Mn-3d in character (Figure 5.8a). The pDOS spectrum shows a sharp peak in the region between -1 to -2 eV, which indicates that these Mn-3d-like bands are relatively flat and unhybridized (the PBEsol band structure is shown in Appendix Figure 5.16). When an on-site U is added (PBEsol + U), these top valence states become significantly more O-2p in character, while the states at lower energy (-5 to -7 eV) become more Mn-3d in character (Figure 5.8b). Thus, the on-site U shifts the O-2p states higher in energy relative to Mn-3d. The peaks in the pDOS at -1 to -2 eV that are observed in PBEsol (Figure 5.8a) are not present in PBEsol + U (Figure 5.8b), which indicates that these bands have greater dispersion when U is applied. Indeed, it can be seen from plots of the band structure that between -1 to -2 eV, the PBEsol bands (Appendix Figure 5.16) are flatter than PBEsol + U (Figure 5.9). The pDOS spectrum computed within PBEsol + U + V (Figure 5.8c) is similar to PBEsol + U , with the main difference being the increase in band gap when adding the inter-site V term (2.0 eV compared to 1.6 eV in PBEsol + U).

When HSE06 is employed, the manifold of states in the region between 0 to -1 eV becomes separated from the rest of the states that are lower in energy (Figure 5.8e). We assign the states in the 0 to -1 eV region to represent the e_g orbitals, while the states

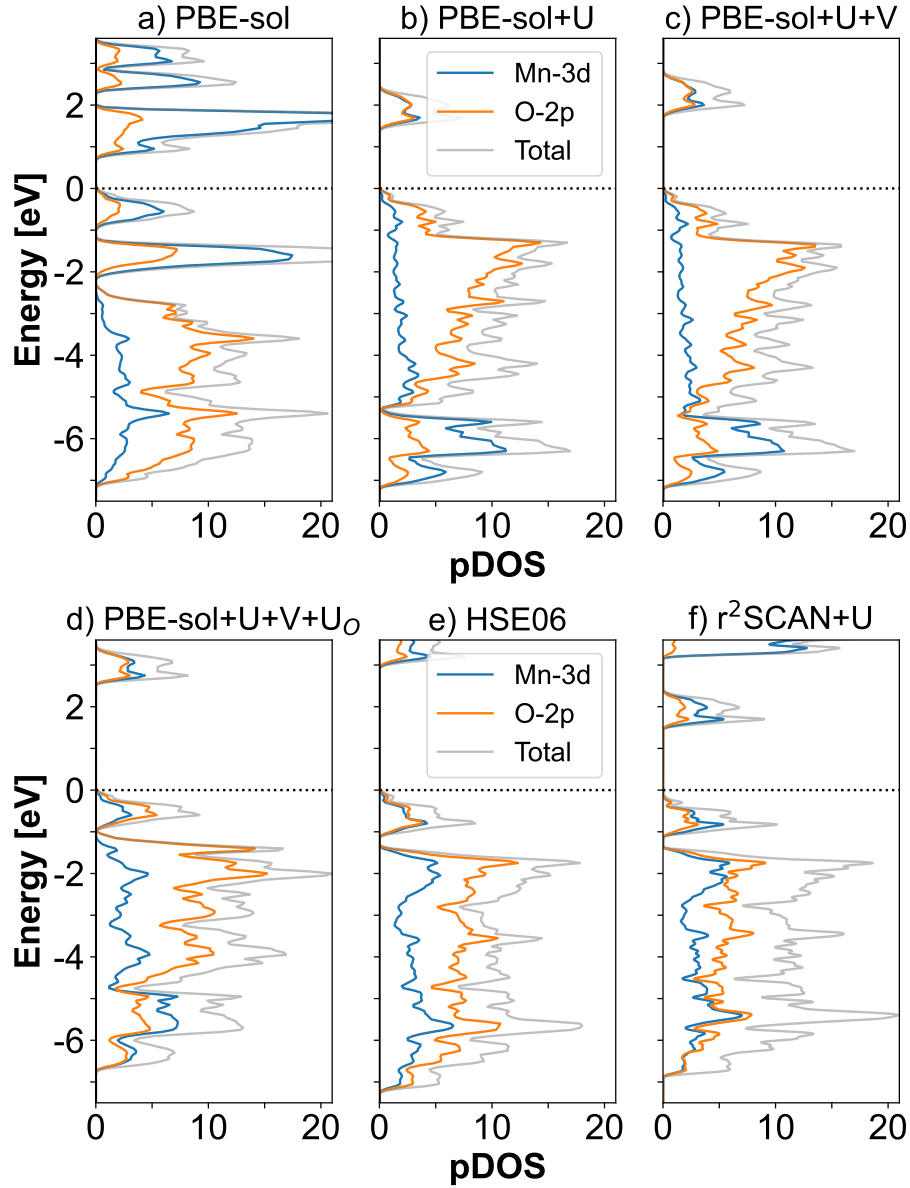


Figure 5.8: Projected density of states (pDOS) of ortho- LiMnO_2 computed using a) PBEsol, b) PBEsol + U , c) PBEsol + U + V , d) PBEsol + $U_{\text{Mn,O}}$ + V , e) HSE06, and f) $r^2\text{SCAN}$ + U . Blue: Mn-3d, orange: O-2p, and grey: total DOS. Energies are referenced to E_F .

lower in energy to be the t_{2g} orbitals, which would be consistent with the crystal field theory of transition metal octahedral complexes. Within this picture, the energy separation between e_g and t_{2g} states represents the crystal field splitting energy (ΔE_{cf}). Within HSE06, the t_{2g} states (from -5 to -7 eV) have slightly more O-2p character than Mn-3d, and

the difference between the two is nearly uniform along the entire energy range. The more uniform distribution of Mn-3*d* and O-2*p*-like states in HSE06 suggests an increased Mn-O hybridization and covalency.

The $r^2\text{SCAN} + U$ pDOS (Figure 5.8f) shows a band gap (1.7 eV) that is substantially smaller than the HSE06 band gap (3.1 eV). However, the occupied manifold of $r^2\text{SCAN} + U$ is in striking agreement with HSE06; in particular, both $r^2\text{SCAN} + U$ and HSE06 display energetically separated e_g and t_{2g} states (i.e. a nonzero ΔE_{cf}) – a feature that is not present neither in PBEsol + U nor in PBEsol + $U + V$. Interestingly, within PBEsol, a nonvanishing ΔE_{cf} can be recovered by applying an additional Hubbard U on the O-2*p* states (see Figure 5.8d – PBEsol + $U_{\text{Mn,O}} + V$). Thus, the manifestation of the crystal field splitting appears to be intimately related to the electronic localization on O-2*p* states.

Since we have assessed a large array of DFT methods, it is important to evaluate the accuracy of each approximation. Given a lack of experimental data on the electronic structure of ortho-LiMnO₂, we perform a one-shot GW (G_0W_0) calculation as a reference point for a realistic description of the electronic structure. The band structure of ortho-LiMnO₂ is computed using PBEsol + U , GW , and HSE06, which are all shown in Figure 5.9. The bands of the majority and minority spin channels are degenerate. To display the differences between the electronic states calculated within GW and its PBEsol + U starting point (i.e. the self-energy corrections), we reference the band energies of these two calculations to E_F of the PBEsol + U calculation in Figures 5.9a and 5.9b.

Within GW (Figure 5.9b), we observe a large renormalization of the PBEsol + U band energies (Figure 5.9a), with self-energy corrections on the order of 1 eV in magnitude, though the values of the self-energies are highly dependent on the band and wave vector. The two empty e_g conduction bands are rigidly shifted upward in energy by ~ 1.2 eV and the valence bands are shifted down by up to > 1 eV compared to PBEsol + U (Figure 5.9a), leading to a significantly larger band gap (3.8 eV) compared to PBEsol + U (1.6 eV). There are more band crossings in the t_{2g} manifold within GW , which highlights the larger dispersion of these bands compared to PBEsol + U . The crystal field splitting ΔE_{cf} is ~ 0.3 eV between the e_g and t_{2g} bands. In PBEsol + U , ΔE_{cf} vanishes as an e_g and t_{2g} band are degenerate at Γ (Figure 5.9a), which is consistent with the PBEsol + U pDOS of Figure 5.8a. The values of ΔE_{cf} and the e_g band widths in GW are close to those in the HSE06 band structure (Figure 5.9c) and $r^2\text{SCAN} + U$ DOS (Figure 5.8f), which validates the electronic structure of the valence states predicted by these DFT functionals.

5.6 Discussion

In this study, we have computed the total energy of the LiMnO₂ polymorphs using several DFT methods and evaluated harmonic phonon contributions to the free energy at finite temperature. Obtaining accurate phase stability trends is not trivial in this system, as precise

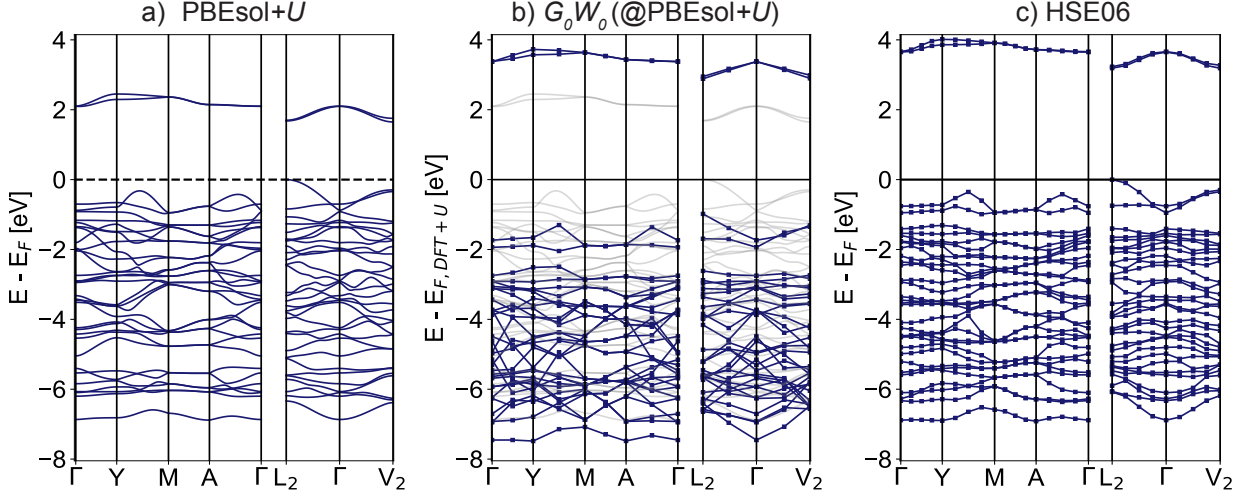


Figure 5.9: Electronic band structure of the ND-refined AFM ortho-LiMnO₂ structure, computed using a) PBEsol + U , b) G_0W_0 (G_0W_0) starting from the PBEsol + U wave functions, and c) HSE06. The majority and minority spin channels are degenerate. In b), the band energies are referenced to the E_F calculated from PBEsol + U and the PBEsol + U band structure is shown in light grey to highlight the GW self-energy corrections. Marked squares in b) and c) indicate the points where the band energies are computed and the lines are linear interpolations between them.

description of the AFM order and interplay between electronic localization/hybridization are required. These effects are inadequately treated within more conventional DFT functionals (e.g. PBEsol + U , r²SCAN, and r²SCAN + U , where values of U are empirically tuned), which lead to the spurious prediction that γ -LiMnO₂ is the ground state. Instead, DFT schemes such as HSE06, PBEsol + U_{sc} (+ V_{sc}), and r²SCAN + U_{sc} are needed to recover ortho-LiMnO₂ as the ground state. Furthermore, these functionals are necessary to predict a disordered layered ordering to be higher in energy than the layered phase, which represents an appreciable anti-site defect formation energy in layered.

We find that an important aspect of the energy difference between all structures arises from the local variation of self-consistently determined Hubbard parameters, especially the on-site U , which is why schemes with averaged Hubbard parameters cannot reproduce the correct phase stability. Specifically, the self-consistent U and V are smallest in the ortho, layered, spinel, and ϵ phases (Table 5.1). These phases all exhibit a collinear ordering of the JT distortions, in which all of the JT axes (and hence the e_g orbitals) are oriented in parallel. Capturing these local variations in electronic interactions in DFT is key for obtaining accurate energetics in this system, and likely would be important for modeling other TM oxides rich in Mn³⁺ or other JT-active ions (e.g. Ni³⁺ and Cu²⁺). HSE06 can also reasonably capture these local differences in the electron-electron interactions despite not

explicitly applying these Hubbard corrections, as it predicts orthorhombic to be the LiMnO_2 ground state. Range-separated hybrid functionals such as HSE06 more rigorously treat the screened electronic exchange interactions as they incorporate a fraction (0.25 in HSE06) of exact Fock exchange to the short-range exchange energy, which can provide an adequate correction to the self-interaction error (SIE) [110, 113]. This indicates that a major source of the errors encountered in applying PBEsol + U and r²SCAN (+ U) is the poor description of electronic exchange, which can be remedied by determining the HP non-empirically.

The differences in formalism of the hybrid-GGA and GGA with self-consistent HPs lead to a different phase stability trend between the γ and ortho phases: within HSE06, γ is only marginally higher in energy (~ 1 meV/atom, Figure 5.3) than ortho- LiMnO_2 , while PBEsol+ $U_{\text{sc}}(+V_{\text{sc}})$ predict a much larger energy difference (> 20 meV/atom). It is difficult to conclude which method is most accurate for this quantity, as there is no known experimental measurement. However, we note that within HSE06, we apply values of the fraction of exact exchange ($\alpha = 0.25$) and range-separation parameter ($\omega = 0.2$) that may not be the optimal values for each LiMnO_2 phase. Methods have been proposed to non-empirically and systematically tune the parameters within hybrid-GGA functionals to more realistically describe the electronic screening and/or minimize the SIE within a given structure [114, 115, 116] – in the same spirit as the calculation of HPs from linear response [122, 125, 129]. Thus, it may be insightful in future studies to evaluate the LiMnO_2 phase stability using a non-empirically tuned hybrid-GGA, though this would come at larger computational cost.

The improved treatment of electronic exchange within HSE06 enables it to more accurately predict the band structure of ortho- LiMnO_2 , as it shows reasonable agreement with the many-body GW method, especially in the band gap and crystal field splitting (ΔE_{cf}) (Figure 5.9). These quantities are more poorly described within PBEsol + $U_{\text{sc}}(+V_{\text{sc}})$, which we have attributed to an insufficient correction of SIE on O-2 p states, which can be alleviated by applying an additional Hubbard U correction on O-2 p states (U_{O}), r²SCAN + U , or HSE06. The values of U_{O} that we calculate from DFPT are ~ 9 eV (Appendix Table 5.7), which are larger than the U values of Mn (~ 6 eV), but in good agreement with previous self-consistent calculations of U_{O} within GGA functionals [130, 215]. The GW and HSE06 methods predict large band gaps (3.8 and 3.1 eV, respectively) that are significantly higher than previously reported calculations [189, 207, 216], and indicate that these phases are strongly insulating.

The electronic structure of these phases are heavily linked to the magnetic order, as the AFM order is shown to increase the covalency of Mn-O bonds, which likely contributes to the significant lowering of energy in each AFM structure relative to the FM state (Figure 5.2c). This enhancement in the hybridization between the Mn-3 d and O-2 p states is correlated with an improved prediction of phase stability (Figure 5.2b). Correlation between AFM interactions and Mn-O covalency is consistent with the theory of AFM "semicovalent exchange", which was initially developed by Goodenough and Loeb to rationalize the an-

tiferromagnetism of various spinel and perovskite phases [217, 218]. Within this theory, a local AFM interaction would lead to the formation of semicovalent bonds between a TM and anion [217, 218, 219, 194]. The large energy difference between FM and AFM states in the ortho and ϵ structures ($\Delta E_{\text{AFM-FM}} \approx -80$ to -100 meV/Mn, shown in Figure 5.2c) suggests that the semicovalent exchange is particularly strong in these phases and is an important factor that helps stabilize them relative to the other LiMnO_2 phases. The ion configurations of ortho and ϵ - LiMnO_2 (Figure 5.1) contain 90° and 180° Mn-O-Mn channels for AFM interactions, whereas layered and spinel only have 90° Mn-O-Mn channels. This structural difference may be why AFM order can have a stronger stabilizing effect on ortho and ϵ compared to the other experimentally-observed layered and spinel phases.

Despite the disparity of phase stability trends observed across various DFT functionals, the energy differences between the experimentally known ortho, layered, and spinel LiMnO_2 phases are surprisingly consistent across each method, which suggests a similarity in the electronic structure of these phases. The PBEsol + $U(+V)$, $r^2\text{SCAN} (+U)$, and HSE06 functionals all predict that the order of DFT total energy from low to high energy is ortho $\rightarrow$ layered $\rightarrow$ spinel, when all structures are in their respective AFM ground state (Figures 5.2b and 5.3). The energy relative to ortho is 5 – 15 meV/atom for spinel and 3 – 8 meV/atom for layered, depending on the functional used. The vibrational free energy of these phases between $T = 0$ to 1000 K are also very similar (Figure 5.4). These observations theoretically confirm that these phases are very thermodynamically competitive across a wide range of temperatures. This thermodynamic competition elucidates why many experimental procedures to synthesize ortho LiMnO_2 can lead to spinel and/or layered impurity phases [199, 201, 200, 202]. Since the energy differences at the LiMnO_2 composition are small, minor off-stoichiometry in Li or Mn content could possibly lead to changes in the phase stability. If this is the case, then the presence of impurity phases may be a result of particles containing off-stoichiometry or following a somewhat different synthesis path. Indeed, it has been previously shown from experiment and computation that upon delithiating layered or ortho LiMnO_2 , there is a driving force to form the spinel phase [31, 189, 204, 220, 221, 222].

Our calculations reveal that the previously unreported ϵ - LiMnO_2 is a potential low-energy phase, since it is predicted to have an energy comparable to all of the experimentally-known phases across all levels of DFT assessed. Specifically, the ϵ structure is consistently predicted to be only ~ 2 meV/atom higher in energy than ortho and lower in energy than layered and spinel. These results may be surprising, as the ϵ cation ordering has never been reported. The low energy of the ϵ phase can be rationalized from its similarities in its structural and electronic properties with ortho, layered, and spinel. Namely, we have shown that ϵ has a collinear ordering of JT axes, comparable Mn magnetic moment, and similar self-consistent Hubbard parameters to these phases.

To further evaluate the structural similarity of the ortho and ϵ phases, we compute their XRD patterns, which are shown in Figures 5.10a and 5.10c, respectively. Both ϵ and ortho-

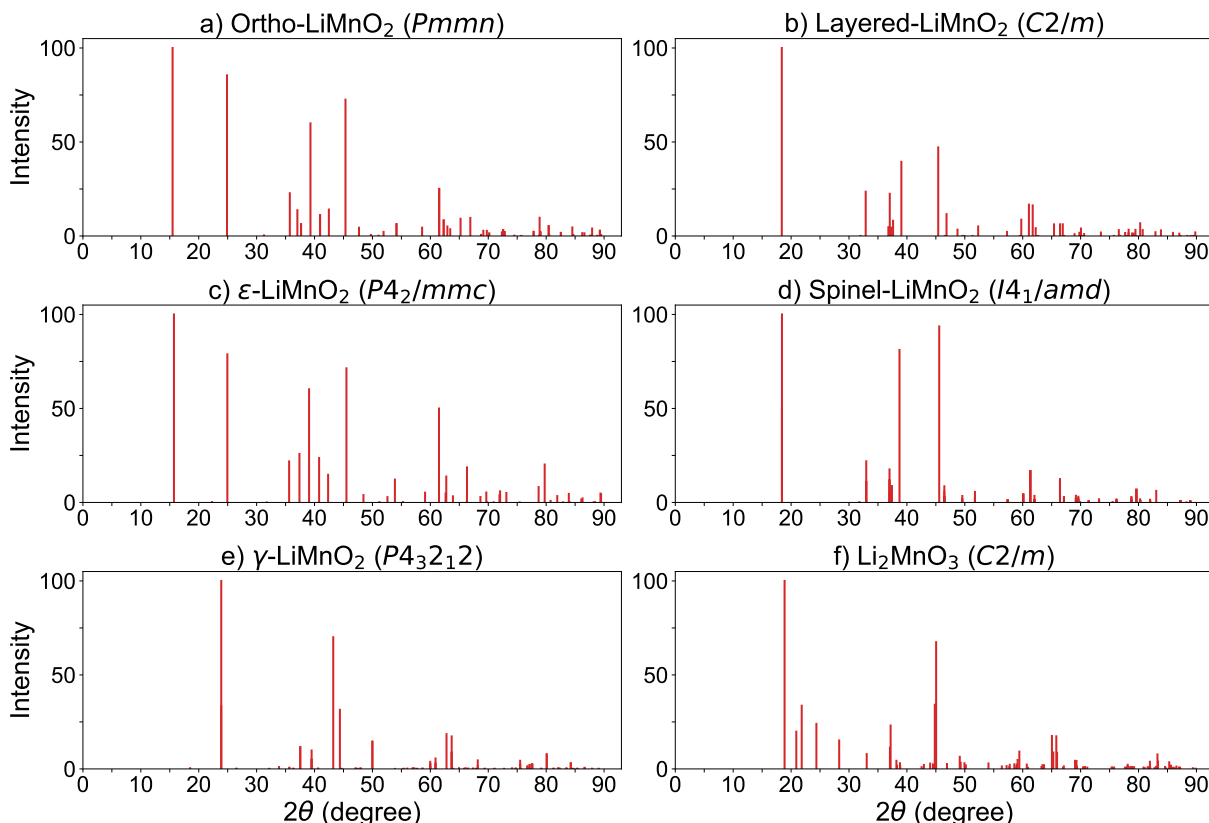


Figure 5.10: Simulated XRD (Cu K- α radiation) patterns of LiMnO_2 and Li_2MnO_3 phases. Each structure is relaxed within HSE06 and the identified space group of the final structure is shown in parentheses.

LiMnO_2 share the same high intensity peaks at $2\theta = 15^\circ$, 25° , 39° , 45° , and 62° . The key differences in these patterns are in the disappearance of one of two peaks at 37° for ϵ , and different relative intensities among the peaks between 35 - 45° . While a low energy above the ground state is no guarantee for synthesizability [223], its similar diffraction pattern compared to ortho may have led ϵ to be missed in previously reported LiMnO_2 samples.

The γ phase is predicted to be the ground state within the PBEsol and $r^2\text{SCAN}$ functionals, with or without averaged Hubbard corrections (Figures 5.2a and 5.2b). Since the γ ordering has never been reported in the LiMnO_2 composition from experiment, we would expect it to be higher in energy than the experimentally-found phases. We simulate the XRD pattern of γ and display it in Figure 5.10e, which clearly does not resemble the XRD patterns of ortho, layered, or spinel (Figures 5.10a, 5.10b, and 5.10d, respectively). Thus, γ would almost certainly not be mistaken for either of these phases, unlike the case of ϵ . The γ structure corresponds to the cation ordering with the lowest electrostatic energy among

Table 5.3: Phonon entropy [k_B /f.u.] of the LiMnO₂ phases as a function of temperature.

Temp. [K]	Ortho	Layered	Spinel	ϵ	γ	Disord. Layered	SQS
300	8.26	8.25	8.29	8.26	7.79	7.94	7.97
600	15.45	15.45	15.49	15.44	14.97	15.14	15.19
900	20.08	20.09	20.13	20.08	19.61	19.78	19.82

LiMO₂ rock salt structures [188]. Hence, the spurious LiMnO₂ ground state prediction is an indication that these methods inadequately capture the specific energy contributions that stabilize ortho-LiMnO₂, and instead overly stabilize electrostatically-favorable configurations. Our results show that the phase stability and electronic structure of LiMnO₂ are more strongly influenced by the subtle balance between electron localization and hybridization, instead of electrostatics. The HSE06, PBEsol + U_{sc} (+ V_{sc}), and r²SCAN + U_{sc} methods appear to provide a more faithful treatment of these aspects, enabling them to correctly predict ortho-LiMnO₂ as the ground state.

Our phonon calculations reveal that γ becomes more unstable relative to ortho as temperature is increased (Figure 5.4), due to its lower vibrational entropy. Disordered layered is also destabilized by its lower phonon entropy, but to a smaller extent than γ . Since γ and disordered layered are the only phases considered that contain noncollinear arrangements of JT distortions, we speculate that the vibrational properties are closely linked to the degree and type of cation and orbital ordering. To further investigate this correlation, we generate a disordered LiMnO₂ special quasi-random structure (SQS) [224] and compare the structural and vibrational properties to the aforementioned LiMnO₂ phases. Upon structural relaxation within PBEsol + U , SQS-LiMnO₂ contains a noncollinear arrangement of JT distortions (structure shown in Appendix Figure 5.18). We compute the phonon entropy (S_{ph}) of SQS-LiMnO₂ as a function of temperature and compare it to the other phases, as presented in Table 5.3. At 300 K, SQS-LiMnO₂ has a very comparable S_{ph} compared to disordered layered and γ . These three phases have a noticeably lower S_{ph} (by 0.3 – 0.5 k_B /f.u.) compared to ortho, layered, spinel, and ϵ -LiMnO₂, which have very similar S_{ph} at 300 K (within 0.05 k_B /f.u. of each other). These trends are consistent across the temperature range examined. These findings suggest that only certain cation configurations can favor the formation of collinear e_g orbital arrangements, which in turn contributes to increasing the S_{ph} .

Since orthorhombic LiMnO₂ is the ground state and also exhibits relatively large S_{ph} , the collinear JT ordering appears to provide a unique source of both electronic and vibrational stability. We speculate that the relatively softer phonon modes in these structures can arise from increased phonon anharmonicity [64] and/or electron-phonon (el-ph) coupling [211, 225], effects that are associated with cooperative JT distortions [194, 226, 227, 228].

Although our employed frozen phonon method does not explicitly account for anharmonicity and el-ph coupling, it may capture small contributions from these effects.

Our findings also indicate that the degree of electron localization and hybridization can be affected by the ordering of JT distortions, as shown by our identification of large variations in self-consistent HPs. The self-consistent Hubbard U in γ is significantly larger than that of the experimentally-known phases (Table 5.1). The values of U are shown to linearly correlate with the Mn magnetic moment (Figure 5.5a). This correlation can be physically intuitive, since when the electron density becomes more confined on Mn-3d orbitals, the strength of the on-site Coulomb interactions (U) between these electrons can naturally increase as well, leading to a larger energy penalty for localization. Greater electron localization on Mn implies a smaller degree of hybridization between Mn and O neighbors, suggesting that the nature of the Mn-O bonding within γ is more ionic, and the bonding within the experimentally-known phases is more covalent. Our calculated electronic pDOS of ortho- LiMnO_2 indeed suggests that the Mn-O bonding in this phase is highly covalent in nature, as there is a strong hybridization of Mn-3d and O-2p states within the valence e_g and t_{2g} manifolds near the Fermi level, especially within r²SCAN + U and HSE06 (Figure 5.8). The disordered layered structure also contains Mn with noncollinear JT distortions and larger values of U , which reflects how the formation of anti-site defects in layered LiMnO_2 can decrease the covalency of some Mn-O bonds. Only the more precise treatments of electronic exchange and correlation within HSE06 and PBEsol + $U_{\text{sc}}(+V_{\text{sc}})$ can reasonably capture the increase in energy arising from reduced Mn-O covalency, which enables the prediction of significant anti-site defect formation energies.

To clarify the impact of orbital ordering on the electronic properties, we calculate the properties of layered LiMnO_2 with a zig-zag arrangement of JT distortions instead of a collinear arrangement – we will refer to this structure as zz-layered LiMnO_2 ($\text{P2}_1/\text{c}$ space group), which is shown in Figure 5.11. The zig-zag ordering of JT axes has been previously studied in layered LiMnO_2 and LiNiO_2 [226, 229]. We calculate the HPs, Mn magnetic moment, and JT bond ratio of zz-layered within PBEsol + $(U + V)_{\text{sc}}$, and compare them to layered LiMnO_2 in Table 5.4. Indeed, we find that zz-layered has a self-consistent Hubbard U that is ~ 170 meV larger than layered LiMnO_2 , as well as a larger magnetic moment. In fact, if we use the line of best fit shown in Figure 5.5a and the computed Mn moment of zz-layered, we can predict a Hubbard U of 6.05 eV, which differs from the self-consistent U only by 0.09 eV. Furthermore, the JT bond ratio of zz-layered is much lower than that of the collinear JT structure, and comparable to γ - LiMnO_2 (Table 5.1). These effects stemming from the collinear JT ordering are thermodynamically favorable, as the computed total energy of the collinear JT ordering is 64 – 140 meV/Mn lower than the zig-zag JT arrangement, depending on the DFT method used. These results provide further evidence that collinear e_g orbital ordering facilitates greater Mn-O covalency and enhances the JT distortion, which results in lowering the total energy.

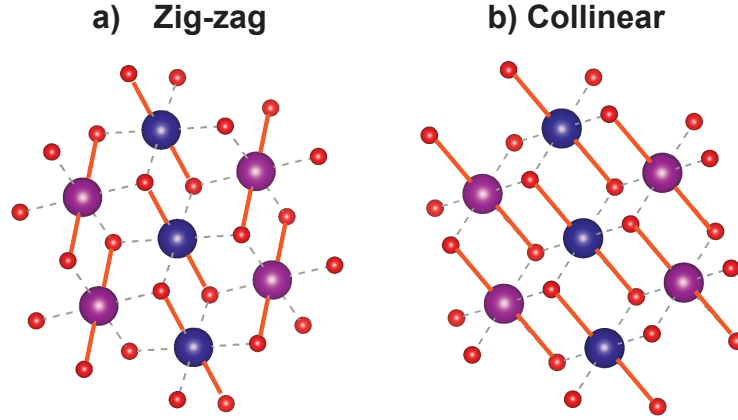


Figure 5.11: Structures of AFM layered LiMnO_2 with a) zig-zag ($P2_1/c$) and b) collinear ($C2/m$) ordering of JT axes. Only one Mn layer is shown for clarity. The JT axes are highlighted in orange. Blue - Mn (up spin), purple - Mn (down spin), and red - O.

Table 5.4: Comparing the properties of layered LiMnO_2 with collinear and zig-zag orderings of JT axes – self-consistent Hubbard parameters, Mn moments, and JT bond ratio ($\frac{\text{long}}{\text{avg. short}}$) within PBEsol + $(U + V)_{\text{sc}}$.

Jahn-Teller Ordering	Hubbard U [eV]	Hubbard V [eV]	Mn Moment [μ_B]	JT bond ratio
Collinear ($C2/m$)	5.79	0.65, 0.30	3.38	1.203
Zig-zag ($P2_1/c$)	5.96	0.68, 0.60, 0.37	3.41	1.147

Our results suggest that the orbital ordering is particularly influential to the phase stability of LiMnO_2 . All structures with a collinear JT ordering exhibit increased covalency of Mn-O bonding, magnitude of JT distortion (Table 5.1), energy differences between the AFM and FM states (up to 100 meV/Mn in ortho and ϵ , shown in Figure 5.2c), and vibrational entropy (Table 5.3). Thus, the JT ordering appears critically linked to several aspects of the electronic and vibrational sources of stability. The LiMnO_2 structures refined from experiment all exhibit the collinear JT ordering [195, 197, 196, 191, 192, 193], which further indicates that this cooperative JT effect is indeed very thermodynamically favorable in LiMnO_2 .

We remark that the stability of the collinear JT ordering and its link to other contributions of the phase stability are not ubiquitous to all TM oxides with JT-active ions. In the low-temperature orthorhombic LaMnO_3 perovskite phase, experimental structural refinements have shown that the JT arrangement is noncollinear [230]. In previous studies of layered LiNiO_2 , DFT (GGA + U) calculations have shown that the noncollinear zig-zag JT

ordering is the ground state orbital arrangement [226, 229]. Radin et al. further showed from GGA + U calculations that the lowering of energy resulting from the JT distortion in layered LiNiO₂ (~ -120 meV/Ni) is much smaller in magnitude than in layered LiMnO₂ (~ -350 meV/Mn) [226]. Furthermore, the stabilizing effect of AFM order in layered LiNiO₂ is predicted to be minimal ($\Delta E_{AFM-FM} \approx -3$ meV/Ni) [226] compared to layered LiMnO₂ ($\Delta E_{AFM-FM} \approx -40$ to -60 meV/Mn), which may be largely due to the higher spin state of the Mn³⁺ electron configuration compared to Ni³⁺.

These discrepancies between layered LiMnO₂ and LiNiO₂ suggest that the contributions to the phase stability of these systems are significantly different. This is indeed reflected in the distinct ground states of these systems — for LiNiO₂ it is the layered structure [229, 188], while for LiMnO₂ it is the orthorhombic phase. The orthorhombic phase is unique, as it is the ground state only for LiMnO₂, while the layered phase is the ground state for many other LiMO₂ compositions ($M = \text{Cr, Co, V, etc}$) [188]. These observations suggest that the LiMnO₂ phase stability is likely dictated by contributions that are unique to this system, and specifically, the Mn³⁺ ion. Our analysis indicates that these contributions are the strong AFM exchange interactions, collinear JT ordering, increased Mn-O covalency, softening of phonon modes, and the coupling between these factors. The strength of JT distortions and AFM interactions are much greater in LiMnO₂ than in LiNiO₂, so we suspect that the strength of these contributions may be unique to LiMnO₂, and indeed helps underpin the unusual phase behavior of this system.

5.7 Implications on other LiMO₂ compositions

To investigate whether the electronic structure challenges encountered for the LiMnO₂ polymorphs (orthorhombic, layered, spinel, γ , ϵ , and disordered layered) are similarly found in other analogous LiMO₂ compositions, we present preliminary findings on the phase stability of the considered structures with compositions $M = \text{Co, Cr, Fe, and Ni}$. The layered R $\bar{3}$ m LiCoO₂ and LiNiO₂ phases have been extensively studied as Li cathodes [17, 7]. The layered phase is known to be the ground state for LiCoO₂, LiNiO₂, and LiCrO₂ [188], while the γ phase is the ground state of LiFeO₂ [205, 231]. For each composition, we calculate the DFT total energy of the considered structures using PBEsol + U , r²SCAN, and r²SCAN + U , using empirically fit U [123, 104] and FM order — with the exception of the LiCoO₂ phases in which we employ nonmagnetic configurations. We note that γ -LiFeO₂ and layered LiCrO₂ are known to be antiferromagnetic at low temperature [232, 231, 233]. The computed energies relative to the layered phase for each composition are shown in Figure 5.12.

We find that for all considered compositions, the layered phase is the predicted ground state, within the given magnetic configurations and DFT functionals. The spinel phase is consistently the second lowest in energy, as it is slightly higher than layered by < 3 meV/atom. This result is physical reasonable for the LiCoO₂, LiCrO₂, and LiNiO₂ compositions, as the layered phase is the known ground state. However, for LiFeO₂, the known ground state is

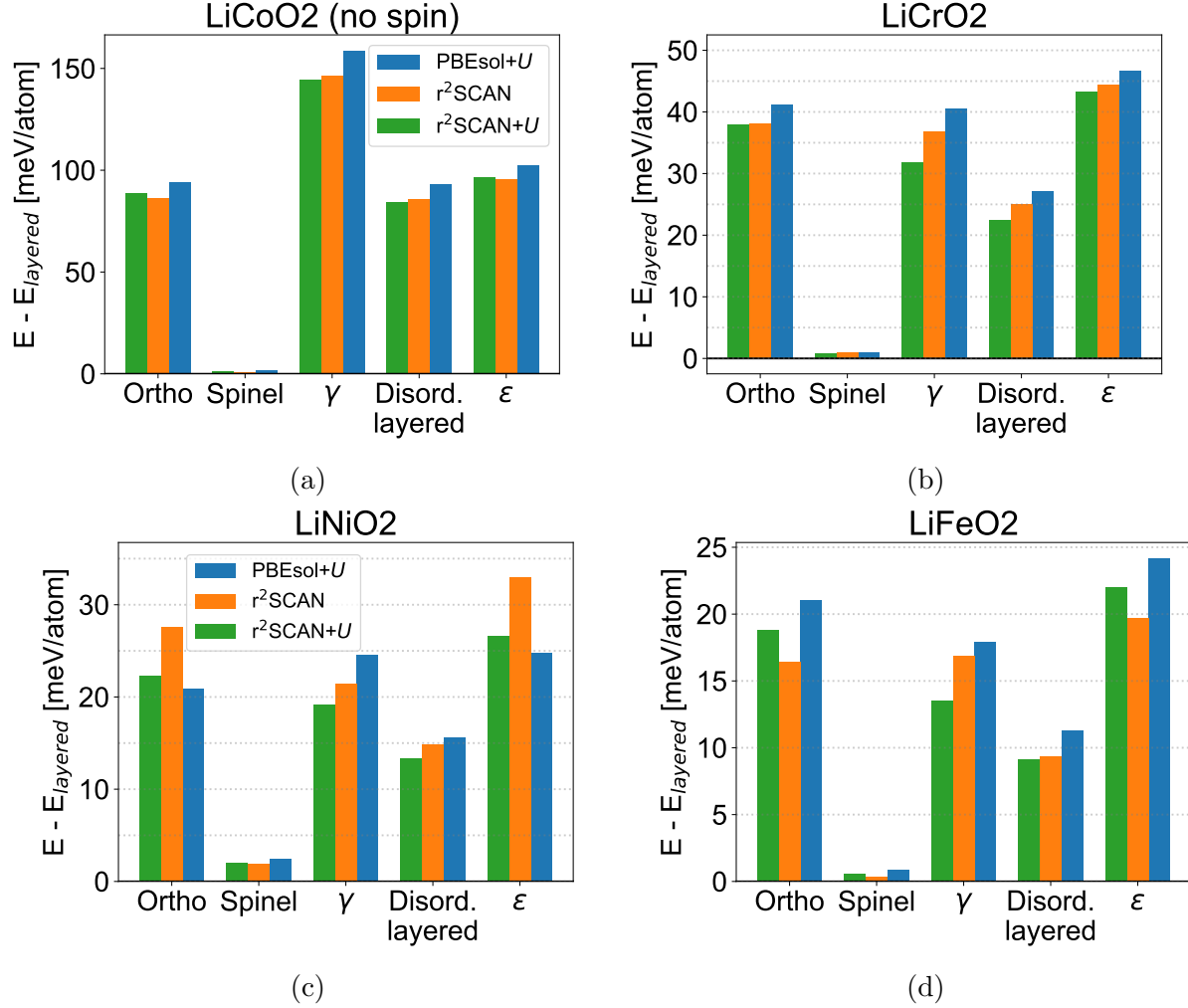


Figure 5.12: DFT energy of LiMO_2 phases ($M = \text{Co, Cr, Ni, Fe}$) relative to the layered phase, calculated using PBEsol + U , $r^2\text{SCAN}$, and $r^2\text{SCAN} + U$ with empirical U . All calculations use FM order, except for the LiCoO_2 calculations which were nonmagnetic.

the γ phase, which is predicted to be 13 – 18 meV/atom higher than layered (Figure 5.12d). Although the layered LiFeO_2 can be synthesized through techniques such as ion exchange, it has been previously concluded to be a metastable phase [205, 234]. It is also remarkable to note that among all considered compositions, the γ phase is the predicted ground state only within LiMnO_2 (Figure 5.2a), using this computational set up.

The ground state prediction errors exhibited within LiMnO_2 and LiFeO_2 likely stem from their high spin electron configurations, as they nominally have the high-spin d^4 and d^5 configurations, leading to DFT-predicted TM magnetic moments of ~ 3.7 and $4.4 \mu_B$,

respectively, which are higher than the other considered LiMO_2 structures. The high-spin configurations would promote stronger magnetic exchange interactions, potentially leading to a strong dependence of the total energy and phase stability on magnetic ordering, as observed within LiMnO_2 (Figure 5.2). Thus, identification of the AFM ground state orderings of each LiFeO_2 phase are likely required for more accurate phase stability predictions. Furthermore, the high spin configurations of Mn/Fe reflect greater electron localization onto each Mn/Fe site, potentially exacerbating the SIE within DFT, which can be remedied by using more precise DFT methods such as hybrid-GGA and GGA with non-empirical HPs. The consideration of magnetic ground states and more precise DFT methods in predicting the phase stability of LiFeO_2 , as well as other strongly (antiferro)magnetic TM oxides, would thus be a potentially insightful direction of future study.

5.8 Conclusion

We have revealed the challenges of modeling the phase stability and electronic structure of the LiMnO_2 polymorphs, and identified avenues for obtaining more accurate results in this system. The degree of electron localization on Mn-3d states is found to vary significantly by phase, and is closely correlated to the self-consistently calculated Hubbard U on Mn-3d states. These values of U can vary by ~ 0.6 eV within PBEsol, and are closely linked to the local JT ordering. More conventional DFT approaches (e.g. GGA and meta-GGA with or without averaged Hubbard corrections) inadequately treat the energy differences arising from subtle changes in electron localization and Mn-O bonding, leading to inaccurate phase stability predictions. Instead, more precise treatments of electronic exchange and correlation (and, especially, screened exchange) within functionals such as HSE06, PBEsol + $U_{\text{sc}}(+V_{\text{sc}})$, and r²SCAN + U_{sc} are required to recover more accurate phase stability – namely the prediction of orthorhombic LiMnO_2 to be the ground state. We expect these DFT methods to be similarly well-equipped to capture the energetics of other TM oxides that are rich in Mn^{3+} or other JT-active ions (e.g. Ni^{3+} and Cu^{2+}).

The ordering of the cations, Mn spins, and e_g orbitals all significantly influence the degree of electron localization and hybridization, which dictate the electronic and vibrational free energy contributions. The collinear arrangement of JT distortions, which is present in ortho, layered, spinel, and ϵ - LiMnO_2 , is shown to simultaneously increase the Mn-O covalency, strength of AFM semicovalent exchange, and vibrational entropy compared to structures with noncollinear JT orderings. The subtle interplay between the electron localization, magnetism, JT distortion, and total energy within the LiMnO_2 phases makes this system a potentially useful test case for benchmarking novel density functional approximations.

An extensive re-examination of the electronic structure of ortho LiMnO_2 reveals the importance of sufficiently correcting the SIE on O-2p states, in addition to Mn-3d states, in order to obtain accurate features of the band structure, such as the crystal field splitting and

band gap. These quantities are well-captured within HSE06, as the predicted band structure is in reasonable agreement with *GW*.

A preliminary assessment of the phase stability of other analogous LiMO_2 compositions suggests that the electronic structure challenges analyzed in LiMnO_2 are not observed in compounds with lower spin TMs (e.g. $M = \text{Co}, \text{Ni}, \text{Cr}$). However, a similar challenge in ground state prediction is encountered for the higher spin LiFeO_2 polymorphs, suggesting the presence of systemic errors in DFT for strongly (antiferro)magnetic TM oxides, which likely stem from the larger SIE in higher-spin TM complexes. A more comprehensive and systematic benchmark of ground state prediction within high-spin TM oxides would thus be an insightful area of future investigation.

5.9 Appendix

Structural relaxations and total energy calculations

The details of the structural relaxations and total energy calculations are listed in Table 5.5. These differences in DFT calculation parameters within VASP are motivated by the PBE-based “MPRelaxSet” and $r^2\text{SCAN}$ -based “MPScanRelaxSet” input sets in pymatgen [50]. The larger cutoffs used within QE calculations compared to VASP are due to the different pseudopotentials used. Within QE calculations, the pseudopotentials are obtained from the Standard Solid-State Pseudopotentials (SSSP) Efficiency PBEsol library (version 1.3.0) and the calculation parameters chosen are consistent with previous studies [81].

Table 5.5: Calculation details of structural relaxations performed within VASP and QE. The Hubbard U , if applied, is imposed on the Mn-3d manifold. All calculations were performed using VASP except for PBEsol+ U + V (QE).

Functional	Pseudo-potentials	Energy cutoff [eV]	Energy conv. [eV]	Forces conv. [eV/Å]	Hubbard U [eV]
PBEsol+ U	PBE-PAW	520	1e-6	1e-2	3.9
$r^2\text{SCAN}$	PBE_52	680	1e-6	2e-2	
$r^2\text{SCAN}$ + U	PBE_52	680	1e-5	2e-2	1.8
HSE06	PBE_52	520	1e-5	3e-2	
PBEsol+ U + V	SSSP v1.3.0 PBEsol eff.	952 (70 Ry)	1.36e-8 (1e-9 Ry)	2e-2 (4e-4 a.u.)	Table I (main text)

Self-consistent calculation of Hubbard parameters

We use density functional perturbation theory (DFPT) as implemented in the **HP** package of **QE** to calculate the Hubbard U and V parameters within PBEsol from first-principles [69,

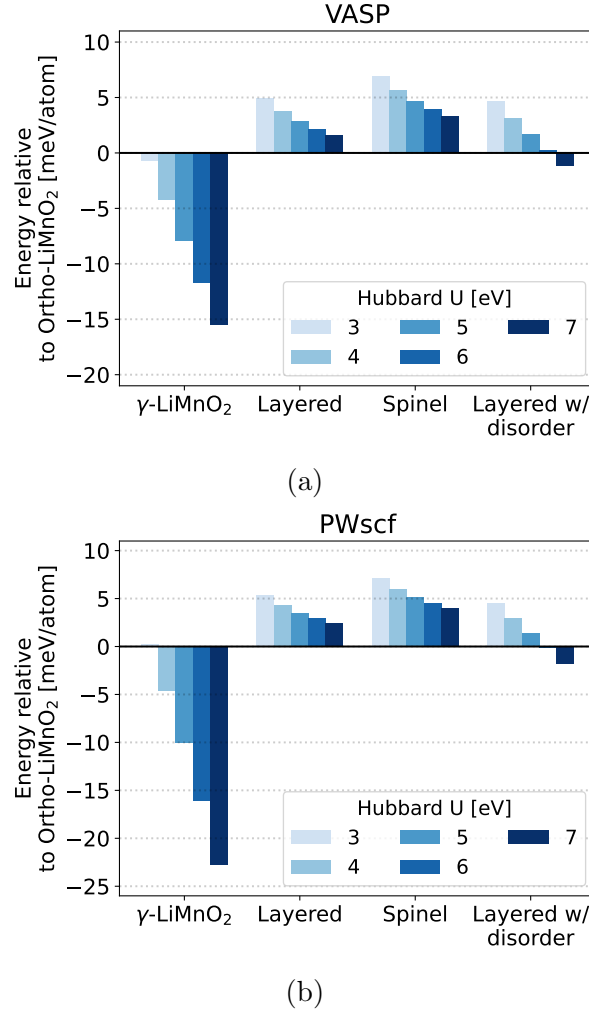


Figure 5.13: Comparison of computed energies of the LiMnO_2 phases relative to orthorhombic LiMnO_2 within PBEsol+ U across a) VASP and b) QE (PWscf). Hubbard U is imposed on Mn-3d manifolds. Each calculation is a SCF calculation.

128]. Lowdin orthogonalized atomic orbitals are used as the Hubbard projectors [208]. The $\mathbf{q}$ -point grids are chosen to be commensurate with a supercell containing lattice parameters that are $> 8 \text{ \AA}$ and the response function is converged to within 10^{-6} atomic units. Each DFPT calculation requires the ground-state electron density and wavefunctions, which are computed from static self-consistent field (SCF) calculations within PBEsol + U + V . In the first iteration, we use $U = 6 \text{ eV}$ and $V = 0.6 \text{ eV}$, and for the subsequent iterations we use the U and V determined from DFPT in the previous iteration. The SCF calculations are converged to within 10^{-12} Ry ($1.36 \times 10^{-11} \text{ eV}$) in the energy. The calculated values of Hubbard U within PBEsol + U_{sc} are systematically larger than in PBEsol + $(U + V)_{sc}$. This

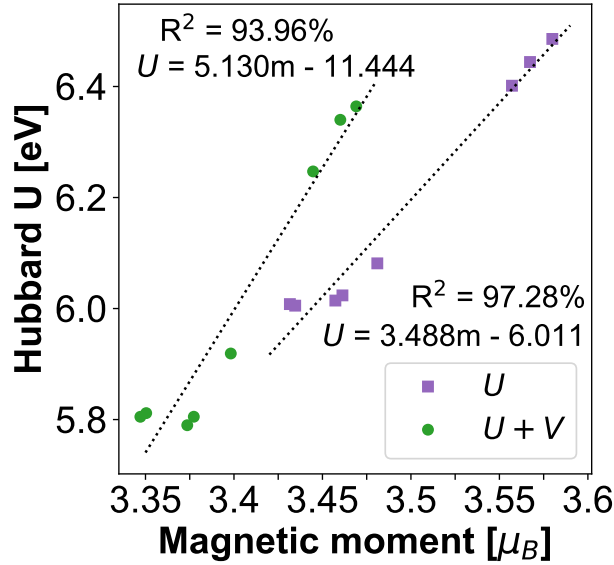


Figure 5.14: Plots of self-consistent Hubbard U and Mn magnetic moments within each LiMnO_2 phase, calculated using $\text{PBEsol} + U_{sc}$ and $\text{PBEsol} + (U + V)_{sc}$. Lines of best fit and R^2 values are also displayed.

leads to a systematic increase in the Mn magnetic moments calculated from $\text{PBEsol} + U_{sc}$ as well. In Figure 5.14, we plot the self-consistent Hubbard U and resulting Mn moments within each phase, using $\text{PBEsol} + U_{sc}$ and $\text{PBEsol} + (U + V)_{sc}$. Although both methods yield a strongly linear relation between self-consistent U and Mn moment, the lines of best fit differ between each method.

For the self-consistent calculations of Hubbard U within r^2SCAN , we use the linear response constrained DFT (LR-cDFT) approach in real-space [122] instead of DFPT, since the current version of **QE** (version 7.4) does not support DFPT calculations in r^2SCAN , as well as other codes to our knowledge. Furthermore, the current version of **QE** does not support variable-cell relaxations within r^2SCAN , so our procedure is to iteratively calculate the self-consistent U using **QE**, then perform structural relaxations using VASP with the self-consistent U . We expect there to be slight incompatibilities with the implementations of Hubbard U between the two codes, which is the main reason why we leave the results in the Appendix. In the LR-cDFT calculations, we create isolated perturbations of the Hubbard manifolds using supercells (of 128 atoms and with each lattice parameter $> 8 \text{ \AA}$) and evaluate the response matrices (χ) of the Hubbard occupations using finite differences. The SCF calculations of the unperturbed and perturbed states are converged to within $1\text{E-}11$ Ry. The current version of **QE** only supports norm-conserving pseudopotentials for r^2SCAN calculations, so we use optimized norm-conserving Vanderbilt (ONCV) PBEsol pseudopotentials selected from the PseudoDojo table [78] (version 0.4.1), since r^2SCAN

Table 5.6: Self-consistent Hubbard U , Mn magnetic moments, and JT bond ratios of the LiMnO₂ phases within r²SCAN and PBEsol, calculated using ONCV pseudopotentials.

Method	Property	Ortho	Layered	Spinel	γ	Disord. layered	ϵ
r ² SCAN + U	U [eV]	4.48	4.46	4.47	4.62	4.45, 4.60, 4.60	4.50
	Mag. moment [μ_B]	3.23	3.26	3.26	3.35	3.27, 3.34, 3.34	3.23
	JT ratio	1.158	1.168	1.165	1.129	1.128, 1.174, 1.120	1.160
PBEsol + U	U [eV]	5.44	5.44	5.45	5.85	5.51, 5.77, 5.83	5.44
	Mag. moment [μ_B]	3.34	3.36	3.36	3.48	3.38, 3.46, 3.47	3.33

norm-conserving pseudopotentials have not yet been generated. We note that these ONCV pseudopotentials are different from the PAW and ultra-soft pseudopotentials (selected from SSSP) used for the PBEsol DFPT calculations, which will contribute to differences in the self-consistent HPs [129, 128]. Thus, we recompute the Hubbard U within PBEsol+ U_{sc} using these ONCV pseudopotentials and compare them to the r²SCAN + U_{sc} values in Table 5.6. The plane-wave basis set cutoff for the LR-cDFT calculations within r²SCAN (using ONCV pseudopotentials) is 55 Ry (748 eV) and 220 Ry (2993 eV) for the charge density. The final calculated total energy of each LiMnO₂ phase within r²SCAN + U_{sc} used plane-wave cutoffs of 70 Ry (952 eV) and 280 Ry (3810 eV) for the charge density. The Hubbard U , Mn magnetic moments, and JT bond ratios computed within r²SCAN and PBEsol using ONCV pseudopotentials are shown in Table 5.6. The Hubbard U calculated within r²SCAN are systematically smaller than PBEsol by ~ 1 eV.

We show the LiMnO₂ phase stability computed within r²SCAN + U_{sc} and compare it to the other DFT methods in Figure 5.15. The γ phase is predicted to be ~ 15 meV/atom higher than ortho, and the disordered layered phase is ~ 10 meV/atom higher than layered, which qualitatively agree with the HSE06 and PBEsol + U_{sc} (+ V_{sc}) results. The energy differences among the ortho, layered, and spinel phases are in excellent agreement among all functionals assessed.

SCF calculations on orthorhombic-LiMnO₂

SCF calculations are performed on the experimentally refined structure of orthorhombic-LiMnO₂ to determine the electronic density of states (DOS), magnetic moments, band gap, and electron density ρ , which are presented in Section 3B-C. An $8 \times 8 \times 8$ $\mathbf{k}$ -point grid is used to sample the Brillouin zone. The functionals used are PBEsol, PBEsol+ U , PBEsol+ U + V , HSE06, and r²SCAN + U ($U = 1.8$ eV). The Hubbard U and V values within PBEsol are re-calculated self-consistently using DFPT at the experimentally refined configuration. The values are $U_{Mn} = 5.81$ eV, $V = 0.76, 0.56$, or 0.38 eV, and $U_O = 9.53$ or 9.27 eV, which are in good agreement with the converged values listed in Table I in the main text. All SCF calculations are performed within QE, except for the r²SCAN + U calculations, which are

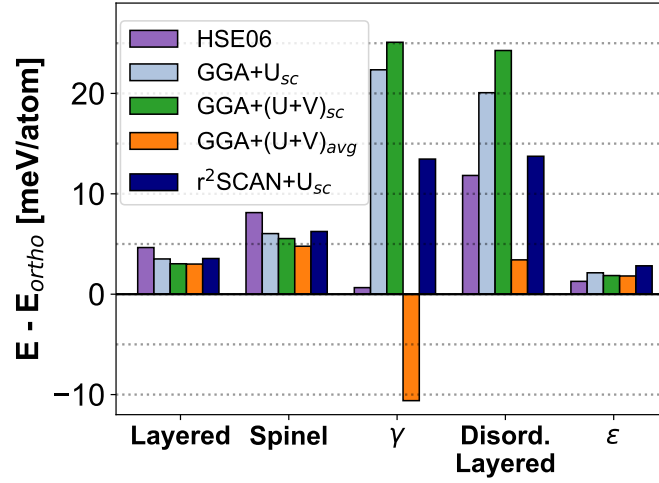


Figure 5.15: DFT energy of each LiMnO_2 phase (with AFM configuration) relative to the orthorhombic phase, within several DFT approximations.

Table 5.7: Hubbard on-site U_{Mn} , U_{O} , and inter-site V ($\text{Mn}3d$ - $\text{O}2p$) parameters in orthorhombic LiMnO_2 , self-consistently calculated using DFPT at the experimentally refined configuration and GGA+ U + V relaxed configuration (also shown in the main text Table I). Only the distinct values are listed. V of the short (1.9-2.0 Å) and long (2.2-2.3 Å) Mn-O bonds are shown in separate rows.

Hubbard Parameter [eV]	Orthorhombic (exp)	Orthorhombic (GGA+ U + V relaxed)
U_{Mn}	5.81	5.81
U_{O}	9.27, 9.53	9.26, 9.55
V (short)	0.76, 0.56	0.72, 0.59
V (long)	0.38	0.38

done in VASP. The HSE06 SCF calculation is performed using optimized norm-conserving Vanderbilt (ONCV) PBEsol pseudopotentials selected from the PseudoDojo table [78] (version 0.4.1) and a plane-wave basis set cutoff of 55 Ry (748 eV). ONCV pseudopotentials are chosen to minimize computational cost, as they are softer than PAWs.

Band structure calculations on orthorhombic- LiMnO_2

The band structure of orthorhombic LiMnO_2 (structure refined from ND) is calculated within PBEsol+ U , HSE06, and (one-shot) GW . The PBEsol+ U band structure is computed using QE and its ground-state wave functions are used as a starting point for the GW calculation.

The PBEsol+ U calculation is performed using ONCV PBEsol pseudopotentials selected from the PseudoDojo table (version 0.4.1)[78] and a plane-wave basis set cutoff of 80 Ry (1088 eV). Norm-conserving pseudopotentials are chosen for these calculations as they are the only form of pseudopotential compatible with the BerkeleyGW package [145]. We re-calculate a self-consistent $U = 5.35$ eV from DFPT, which is different from the value calculated using SSSP pseudopotentials. Variations in Hubbard parameters calculated using different pseudopotentials are expected [128]. The HSE06 band structure is computed using VASP, due to the lower computational cost compared to QE. The reciprocal space discretization is chosen such that 3 $\mathbf{k}$ -points separate each high symmetry point along the selected path through the Brillouin zone.

GW calculations of the orthorhombic LiMnO_2 band structure are performed using BerkeleyGW [144, 145]. The static dielectric matrix (ϵ) is computed within the random phase approximation using a $4 \times 4 \times 4$ $\mathbf{q}$ -point grid with a small shift of $0.001\hat{z}$. The static ϵ is extended to finite frequencies using the Hybertsen-Louie plasmon pole model [144]. A plane-wave cutoff of 80 Ry (1088 eV) and 1000 bands (60 occupied, 940 unoccupied) are used to generate PBEsol + U orbitals on a $4 \times 4 \times 4$ $\mathbf{k}$ -point grid.

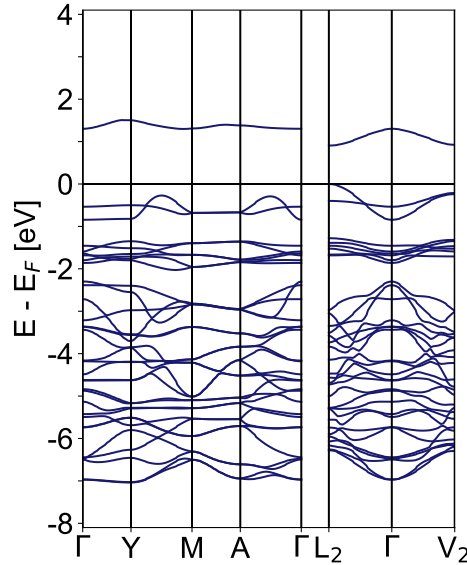


Figure 5.16: Band structure of the experimentally refined ortho- LiMnO_2 structure computed within PBEsol.

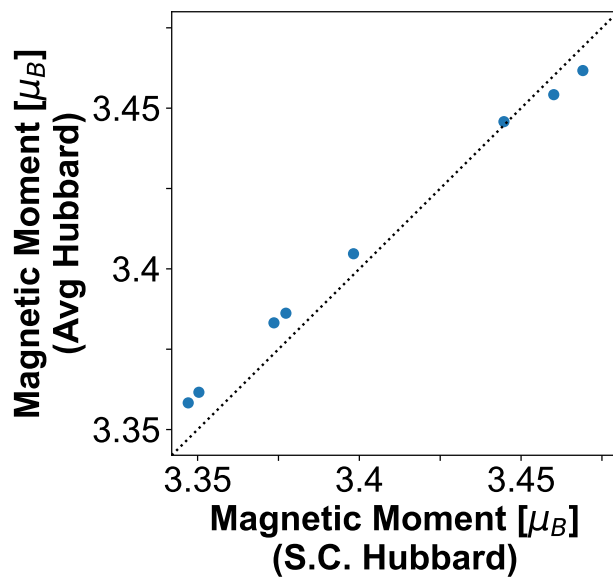


Figure 5.17: Comparing the Mn magnetic moments computed using PBEsol with self-consistent (sc) HPs and averaged (avg) HPs.

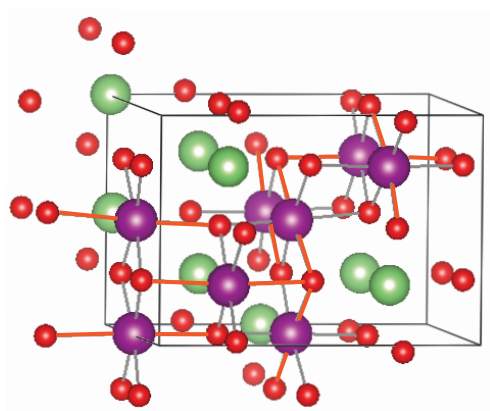


Figure 5.18: Special quasi-random structure of LiMnO_2 relaxed with PBEsol + U . JT axes are labeled in orange. Purple: Mn, green: Li, red: O.

Chapter 6

Phase Diagram of Li-Mn-Ti-O Rock-Salt Phases

6.1 Introduction

Cation disordered rock-salt with Li-excess (DRX) cathode materials are a particularly promising class of Li cathode materials that utilize earth abundant elements and can deliver high energy density that rivals state-of-the-art Ni-Mn-Co (NMC) cathodes [235, 20, 21, 22, 23, 236]. The Li-Mn-Ti-O (LMTO) composition space has been a fruitful source of candidate DRX compositions, such as $\text{Li}_{1.2}\text{Mn}_{0.4}\text{Ti}_{0.4}\text{O}_2$ and $\text{Li}_{1.05}\text{Mn}_{0.85}\text{Ti}_{0.1}\text{O}_2$ [235, 20, 22, 23, 237, 238, 239, 240, 241]. More recently, it has been found that Mn-rich LMTO compositions such as $\text{Li}_{1.05}\text{Mn}_{0.85}\text{Ti}_{0.1}\text{O}_2$ are especially promising, as they tend to transform to δ -DRX phases with anti-phased nanoscale spinel domains upon electrochemical cycling or chemical delithiation, leading to improved power density [235, 240, 242, 243, 244].

DRX compositions with high Mn fraction are typically prepared using conventional solid-state synthesis at relatively high temperatures ≥ 1000 °C [20, 21, 22, 241]. Recently, Patil et al. showed that LMTO DRX compositions containing relatively higher fractions of Li and Ti, such as $\text{Li}_{1.2}\text{Mn}_{0.4}\text{Ti}_{0.4}\text{O}_2$, can be prepared at lower temperatures ~ 800 °C through sol-gel synthesis [241]. Other strategies such as molten-salt [245] and microwave synthesis [246] have also been developed. The synthesis conditions have a strong impact on particle size and short-range order, which in turn affect the electrochemical kinetics of (δ -)DRX [235, 243]. For example, at high temperature the particles can grow very quickly and inhomogeneously, leading to poor electrochemical kinetics [243]. Thus, it is favorable to lower DRX synthesis temperatures, as well as optimize other synthesis conditions such as the holding times and heating/cooling rates. It becomes vital then to understand the minimum temperatures at which DRX becomes thermodynamically stabilized (i.e. the order-disorder transition temperature — which we will refer to as T_{disord}), and assess the possible composition dependence of T_{disord} .

Since DRX is a disordered phase, it is expected to be stabilized at elevated temperature by its increased configurational entropy (S_{config}). Meanwhile, the enthalpic (H) contribution to the free energy is more favorable for the ordered ground states. The balance between S_{config} and H contributions determines the T_{disord} and stability of DRX relative to the ordered phases. The S_{config} can be significantly influenced by the number of distinct species and their fractions present within a given composition, as well as the tendency of certain species to form short-range order. The enthalpy of DRX can be significantly lowered by adding ions with the d^0 electron configuration (such as Ti^{4+}), since the d^0 electronic structure can accommodate local lattice distortions at minimal energy cost, as previously shown by Urban et al. [247].

The objective of our study is to derive a phase diagram of LMTO rock-salt-type phases, using a combination of *ab initio* thermodynamics and experiments. As shown in Figure 6.1a, we span the pseudo-ternary of $\text{LiMnO}_2 - \text{Li}_2\text{MnO}_3 - \text{Li}_2\text{TiO}_3$ compositions. Previous experiments have shown that the ordered phases that are stable at ambient temperature are the orthorhombic LiMnO_2 phase [190, 195, 220], layered Li_2MnO_3 [248, 249], and layered Li_2TiO_3 [250, 251, 252]. The orthorhombic LiMnO_2 (Pmmn) structure exhibits corrugated layers of Mn or Li that alternate with each other, which we note is unique because other analogous LiMO_2 compositions (where M can be a single species or an admixture of species) typically crystallize in a layered $R\bar{3}m$ structure [188]. The unique stability of the orthorhombic Pmmn structure has been attributed to the cooperative Jahn-Teller (JT) distortion of Mn^{3+} ions, which lowers the total energy by breaking the degeneracy of the single half-filled e_g states of Mn^{3+} ions. In layered Li_2MnO_3 , the Mn are nominally in the +4 oxidation state with unfilled e_g states, so they do not exhibit a JT distortion. The layered Li_2MnO_3 and Li_2TiO_3 phases are nearly isostructural in that they consist of alternating planes of Li and $D_2\text{Li}$ (where D can either be Mn or Ti), with the D atoms arranged in honeycombs surrounding each Li. Layered Li_2TiO_3 has been reported to crystallize with the C2/c space group, while Li_2MnO_3 has been reported to have either C2/c or C2/m symmetry [248, 249, 253], with these differences in symmetry arising from distinct stacking patterns of the honeycomb-ordered $D_2\text{Li}$ layers [249]. Within our first-principles calculations, we find that the C2/m and C2/c stacking patterns yield nearly identical total energies (within 0.6 meV/atom) for Li_2MnO_3 and Li_2TiO_3 , consistent with previous work on Li_2MnO_3 [254].

Since the nominal oxidation states of Mn in LiMnO_2 and Li_2MnO_3 are +3 and +4, respectively, the compositions along the $\text{LiMnO}_2 - \text{Li}_2\text{MnO}_3$ pseudo-binary (Figure 6.1a) are expected to contain Mn^{3+} , Mn^{4+} , and excess Li (relative to LiMnO_2) in ratios that preserve charge neutrality, as described by the expression $\text{Li}_{1+x}\text{Mn}_{1-3x}^{3+}\text{Mn}_{2x}^{4+}\text{O}_2$, where x is the fraction of excess Li (per O_2) relative to LiMnO_2 and spans the range $0 \leq x \leq 1/3$. Compositions along the $\text{LiMnO}_2 - \text{Li}_2\text{TiO}_3$ pseudo-binary can be described by an analogous expression $\text{Li}_{1+x}\text{Mn}_{1-3x}^{3+}\text{Ti}_{2x}^{4+}\text{O}_2$. The third axis of the LMTO pseudo-ternary is the replacement of Mn^{4+} with Ti^{4+} ($\text{Li}_2\text{Mn}_{1-y}^{4+}\text{Ti}_y^{4+}\text{O}_3$ – Figure 6.1a). Considering all compositional constraints, the LMTO rock-salt compositions can be described by the expression $\text{Li}_{1+x}\text{Mn}_{1-x-y}\text{Ti}_y\text{O}_2$, where

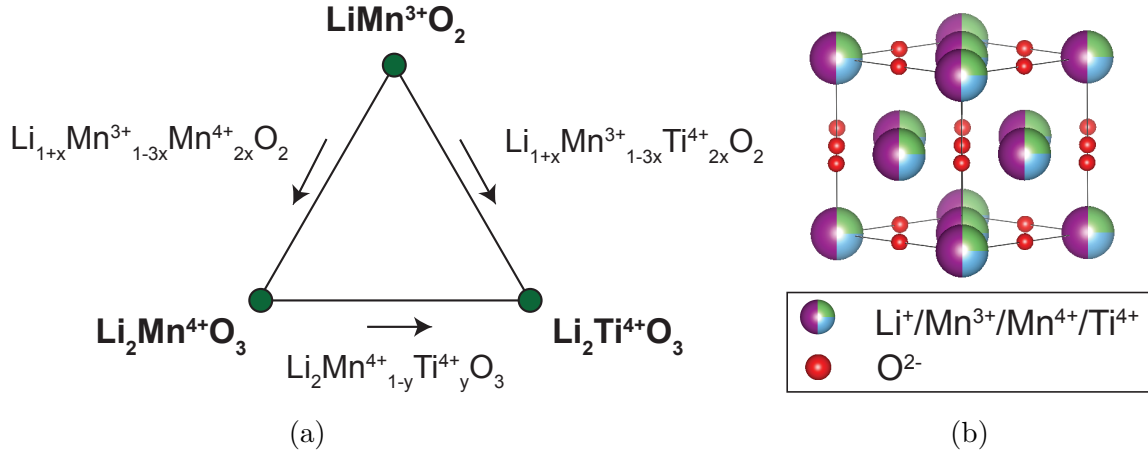


Figure 6.1: Composition and configuration space of the LMTO rock-salt phases. a) Pseudo-ternary $\text{LiMnO}_2 - \text{Li}_2\text{MnO}_3 - \text{Li}_2\text{TiO}_3$ composition space. Nominal TM oxidation states and changes in composition along the edge pseudo-binary lines are labeled. b) Unit cell of the FCC rock-salt lattice, with octahedral cation sites that can be occupied by Li^+ , Mn^{3+} , Mn^{4+} , or Ti^{4+} .

$0 \leq x \leq \frac{1}{3}$ and $0 \leq y \leq 2x$. All possible structures within the LMTO rock-salt space represent distinct cation arrangements (Li^+ , Mn^{3+} , Mn^{4+} , or Ti^{4+}) on a face-centered-cubic (FCC) lattice of octahedral sites. The unit cell of the rock-salt framework is shown in Figure 6.1b.

The most important aspect of our study is to understand the stability of the DRX phase by mapping T_{disord} as a function of composition. From first-principles modeling, we account for the electronic and configurational free energy contributions, by harnessing the cluster expansion (CE) and Monte Carlo (MC) sampling approach [35, 184, 34], which have been extensively applied to study the thermodynamics of a wide range of disordered materials systems spanning battery cathodes [56, 55, 57], alloys [255, 46], magnetic materials [256, 257], and more. We train a CE model to describe the energetics of the quaternary configuration space of cation sites (Figure 6.1b). We distinguish between the +3 and +4 states of Mn as it has been shown by Zhou et al. that the "configurational electronic" entropy of a species in different oxidation states can be critical for stabilizing solid-solution phases in ionic materials such as $\text{Li}_x\text{Fe}_x^{2+}\text{Fe}_{1-x}^{3+}\text{PO}_4$ [258].

To accurately compute the LMTO phase diagram, the CE model must be trained on density-functional theory (DFT)-computed total energies that realistically describe the energetics of the possible structures — and most crucially, reproduce the correct ground states. In Chapter 5, we have shown that commonly utilized DFT approaches such as GGA (PBEsol [95]) and meta-GGA ($r^2\text{SCAN}$ [101]) functionals, with or without empirical Hubbard U corrections [106], spuriously predict the ground state of LiMnO_2 to be the γ - LiMnO_2 polymorph

(isostructural to γ -LiFeO₂ [205]), which has never been reported in experiment [259]. Meanwhile, the HSE06 hybrid-GGA functional [113] can correctly predict the orthorhombic phase to be the LiMnO₂ ground state. Thus, we use HSE06 to calculate the total energy of each structure to train our CE model (more details in Appendix chapter 6.6). We note that HSE06 requires significantly more computational resources compared to GGA and meta-GGA functionals, which is the main reason why most previous studies involving DFT and CE calculations of LMTO phases have employed GGA or meta-GGA-based techniques [56, 55, 57]. The failures of the PBEsol and r²SCAN-based methods to predict the correct LiMnO₂ ground state properties have been attributed to the complex interplay between JT distortions, electronic localization, and antiferromagnetism of Mn³⁺ ions, which the HSE06 functional can capture with better accuracy due to the more precise treatment of screened electronic exchange interactions within the hybrid-GGA formalism [259]. This helps reduce self-interaction and delocalization errors within DFT that can be large when treating correlated 3d electron states [106, 113, 122]. Furthermore, accounting for AFM order was shown in previous studies to significantly lower the energy of each LiMnO₂ phase compared to the ferromagnetic (FM) state and improve LiMnO₂ phase stability predictions [259, 189], so we also search for the lowest energy AFM ordering for each ion configuration within PBEsol+*U*, using a previously developed DFT workflow [209, 31].

By calculating the energies of each LMTO structure using the HSE06 functional (more details in Appendix chapter 6.6), we can reasonably capture the complex electronic structure of the LMTO phases (especially near the LiMnO₂ composition) and curate a DFT data set that contains the physically correct ground states. A CE model is parameterized on this DFT data, which recovers the known LMTO ground states. The CE is then harnessed to perform MC sampling and thermodynamic integration to compute the free energies of the competing ordered and disordered LMTO phases, and determine the phase boundaries between them (more details in Methods).

We perform a complementary set of experiments utilizing heating and *in situ* X-ray diffraction (XRD) measurements within an inert environment to track the phase evolution as a function of temperature for specific LMTO compositions along the LiMnO₂ – Li₂TiO₃ and LiMnO₂ – Li₂MnO₃ pseudo-binary composition axes (Figure 6.1a). For each composition, we quantify the temperature at which DRX becomes phase-pure (which we define as T_{disord}) and identify the ordered phases that form below T_{disord} . The experiments are performed under an inert environment to prevent oxidation of the samples, which can lead to the formation of undesired phases such as spinel LiMn₂O₄ [222, 202]. A similar heating and *in situ* XRD set-up has recently been used by Liang et al. to rationalize the reaction mechanisms leading to DRX formation in the fluorinated Li_{1.1}Mn_{0.8}Ti_{0.1}O_{1.9}F_{0.1} composition [260]. We also perform quenching of select compositions from temperatures near T_{disord} .

We identify the LMTO phase diagram to be a eutectoid-like phase diagram, in which the T_{disord} decreases upon introducing off-stoichiometry to the end-point phases (orthorhombic

LiMnO_2 , layered Li_2TiO_3 , and layered Li_2MnO_3). Importantly, introducing small to moderate amounts of Li-excess, Ti^{4+} , and/or Mn^{4+} (relative to LiMnO_2) can lead to T_{disord} values that are significantly lower than typically used DRX synthesis temperatures (≥ 1000 °C). In general, the results of our calculations agree well with experiments. However, in experiments on compositions with a small amount of Li excess compensated by Mn^{4+} , we observe a layered LiMnO_2 -like phase to form. Our calculations do not predict this phase to be thermodynamically stable, suggesting it is a metastable phase that can form more rapidly than the thermodynamically predicted phase separation upon cooling.

6.2 LMTO phase diagram

To construct our DFT dataset of LMTO rock-salt structures, we enumerate structures across the pseudo-ternary $\text{LiMnO}_2 - \text{Li}_2\text{MnO}_3 - \text{Li}_2\text{TiO}_3$ composition space, with the sampled compositions shown in Figure 6.2a. Many of these structures were generated by introducing off-stoichiometry and/or anti-site defects to the ordered LMTO ground states (orthorhombic LiMnO_2 , layered Li_2MnO_3 , layered Li_2TiO_3), as well as other low-energy ordered LiMnO_2 phases such as layered, spinel, and γ - LiMnO_2 . Disordered configurations are also sampled from MC simulations at elevated T across various LMTO compositions. An internal database of LMTO rock-salt structures compiled in previous studies is also used [56, 55, 57]. In all, we gather 745 unique cation configurations in the LMTO rock-salt lattice and calculate their formation energies at $T = 0$ K using the HSE06 hybrid-GGA functional. The compositions and energies are shown as color-coded squares in Figure 6.2a. With the exception of the end-point ground state phases, we do not identify any additional LMTO structures that are predicted to be stable at $T = 0$ K from DFT, as all enumerated structures have positive energies above the hull (E_{hull}).

To provide a more quantitative visualization of the energy landscape, we plot the formation energies within the pseudo-binary $\text{LiMnO}_2 - \text{Li}_2\text{TiO}_3$ ($\text{Li}_{1+x}\text{Mn}_{1-3x}^{3+}\text{Ti}_{2x}^{4+}\text{O}_2$) and $\text{LiMnO}_2 - \text{Li}_2\text{MnO}_3$ ($\text{Li}_{1+x}\text{Mn}_{1-3x}^{3+}\text{Mn}_{2x}^{4+}\text{O}_2$) axes in Figures 6.2c and 6.2d, respectively. The Li-excess structures within $\text{Li}_{1+x}\text{Mn}_{1-3x}^{3+}\text{Ti}_{2x}^{4+}\text{O}_2$ can have significantly lower values of E_{hull} compared to the $\text{Li}_{1+x}\text{Mn}_{1-3x}^{3+}\text{Mn}_{2x}^{4+}\text{O}_2$ space. For example, there are many $\text{Li}_{1+x}\text{Mn}_{1-3x}^{3+}\text{Ti}_{2x}^{4+}\text{O}_2$ structures with $E_{\text{hull}} \lesssim 10$ meV/atom, while there are no $\text{Li}_{1+x}\text{Mn}_{1-3x}^{3+}\text{Mn}_{2x}^{4+}\text{O}_2$ structures with $E_{\text{hull}} < 10$ meV/atom. The structures with lowest E_{hull} are the layered LiMnO_2 , orthorhombic LiMnO_2 , γ - LiMnO_2 , spinel LiMnO_2 , and layered $\text{Li}_2\text{MnO}_3/\text{Li}_2\text{TiO}_3$ phases with off-stoichiometry.

We assign oxidation states to the Mn atoms in each LMTO structure based on the absolute values of the Mn magnetic moments ($|m_{\text{Mn}}|$) computed within HSE06, a histogram of which is shown in Figure 6.2b. We find a clearly bimodal distribution of $|m_{\text{Mn}}|$ with peaks centered at $|m_{\text{Mn}}| = 3.0$ and $3.7 \mu_B$. By assigning all higher spin Mn with $|m_{\text{Mn}}| > 3.35 \mu_B$ to be Mn^{3+} and Mn with $|m_{\text{Mn}}| \leq 3.35 \mu_B$ to be Mn^{4+} , the number of structures that are formally charge-neutral is maximized [56]. The average $|m_{\text{Mn}}|$ of Mn^{3+} and Mn^{4+} that we calculate within the HSE06 functional are in reasonable agreement with previous studies

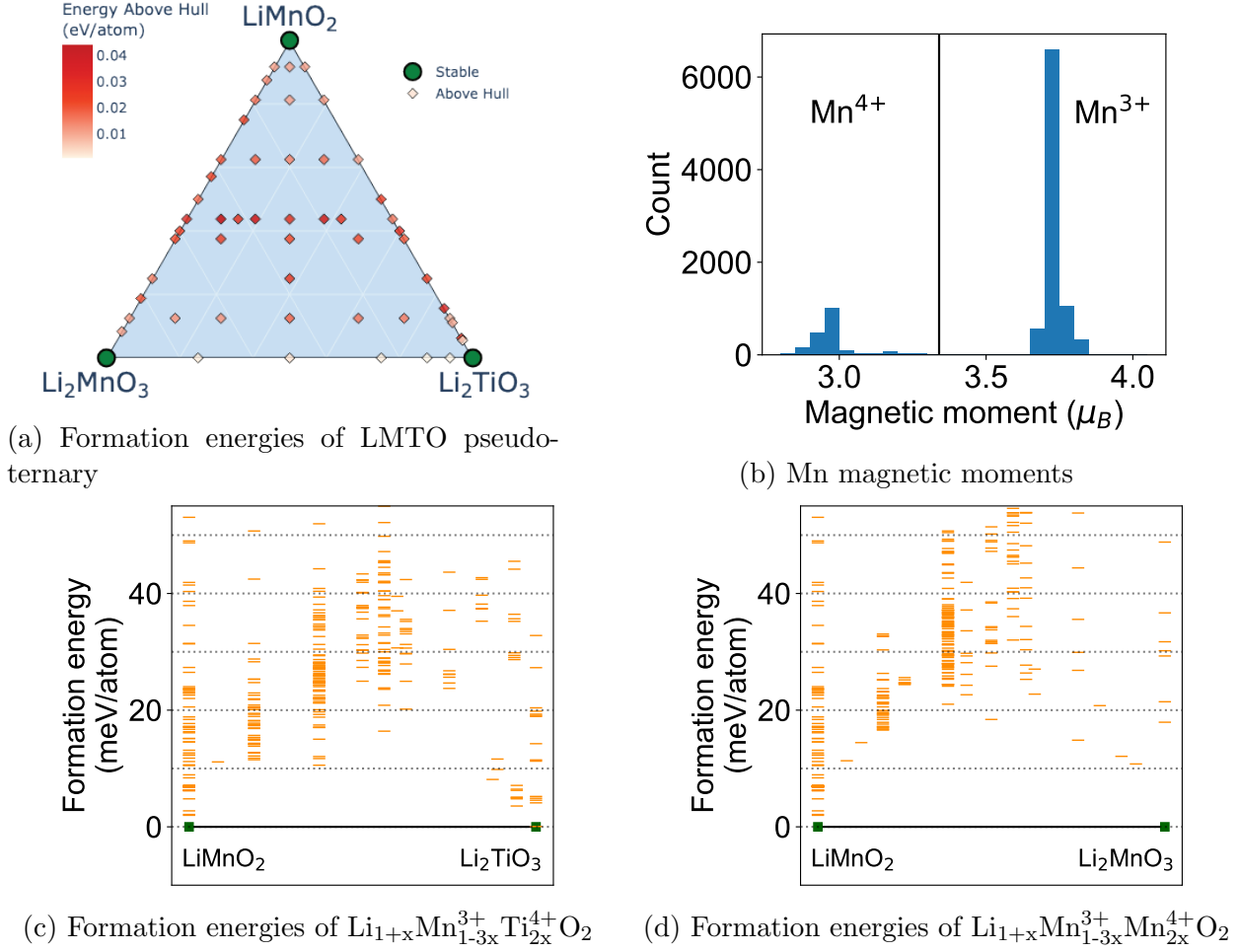


Figure 6.2: DFT-computed formation energies at 0 K and Mn magnetic moments of the training set of LMTO rock-salt orderings. a) Formation energies of structures within the LMTO pseudo-ternary — specifically the lowest energies of each sampled composition. Green circles represent stable phases and squares represent configurations with energy above the convex hull. b) Histogram of absolute values of Mn magnetic moments ($|m_{\text{Mn}}|$). The vertical line at $|m_{\text{Mn}}| = 3.35 \mu_B$ denotes the threshold between Mn^{3+} and Mn^{4+} , with all Mn with $|m_{\text{Mn}}| > 3.35 \mu_B$ assigned to be Mn^{3+} , while Mn with $|m_{\text{Mn}}| < 3.35$ assigned as Mn^{4+} . Formation energies along the pseudo-binary c) LiMnO_2 - Li_2TiO_3 ($\text{Li}_{1+x}\text{Mn}_{1-3x}^{3+}\text{Ti}_{2x}^{4+}\text{O}_2$) and d) LiMnO_2 - Li_2MnO_3 ($\text{Li}_{1+x}\text{Mn}_{1-3x}^{3+}\text{Mn}_{2x}^{4+}\text{O}_2$) composition lines, where green squares are stable phases and orange lines are configurations above the convex hull.

[35, 56] that utilized meta-GGA (SCAN or $r^2\text{SCAN}$) functionals, though our $|m_{\text{Mn}}|$ values computed within HSE06 are systematically slightly higher and the distribution more discrete (less continuous). These differences in our calculated $|m_{\text{Mn}}|$ compared to previous studies can be attributed to the reduced self-interaction error (SIE) of the HSE06 hybrid-GGA

functional, which helps enforce greater electron localization onto the Mn-3d states compared to meta-GGA methods. The calculated magnetic moments of all Ti atoms are near zero (within $0.01 \mu_B$), which confirms that all Ti are in the +4 oxidation state.

To understand the phase stability at elevated temperature, we parametrize a CE on the DFT energies of the LMTO rock-salt structures and perform MC simulations and thermodynamic integration to map the phase diagram of this system. Our trained CE model correctly recovers the DFT-predicted ground states, as shown in Appendix Figure 6.11. We specifically analyze the pseudo-binary spaces of $\text{LiMnO}_2 - \text{Li}_2\text{TiO}_3$ ($\text{Li}_{1+x}\text{Mn}_{1-3x}^{3+}\text{Ti}_{2x}^{4+}\text{O}_2$), $\text{LiMnO}_2 - \text{Li}_2\text{MnO}_3$ ($\text{Li}_{1+x}\text{Mn}_{1-3x}^{3+}\text{Mn}_{2x}^{4+}\text{O}_2$), and $\text{LiMnO}_2 - \text{Li}_2\text{Mn}_{0.5}\text{Ti}_{0.5}\text{O}_3$ ($\text{Li}_{1+x}\text{Mn}_{1-3x}^{3+}\text{Mn}_x^{4+}\text{Ti}_x^{4+}\text{O}_2$). By examining these select pseudo-binary systems, we can quantitatively analyze the influence of Li-excess (x) and type/concentration of the +4 ion (which we will refer to as D^{4+} , where D can either be Mn or Ti) towards stabilizing the DRX phase. We calculate the temperature – composition phase diagrams of $\text{Li}_{1+x}\text{Mn}_{1-3x}^{3+}\text{Ti}_{2x}^{4+}\text{O}_2$, $\text{Li}_{1+x}\text{Mn}_{1-3x}^{3+}\text{Mn}_{2x}^{4+}\text{O}_2$, and $\text{Li}_{1+x}\text{Mn}_{1-3x}^{3+}\text{Mn}_x^{4+}\text{Ti}_x^{4+}\text{O}_2$, and plot them along with the T_{disord} determined from *in situ* XRD experiments (gold stars) in Figure 6.3.

Within the $\text{Li}_{1+x}\text{Mn}_{1-3x}^{3+}\text{Ti}_{2x}^{4+}\text{O}_2$ pseudo-binary phase diagram (Figure 6.3a), the calculated T_{disord} of LiMnO_2 is 1200°C , which is in reasonable agreement with experiment (1070°C). As the Li and Ti concentration increases, T_{disord} linearly decreases until a predicted eutectoid point at $T_{\text{eutec}} = 700^\circ\text{C}$ and $x_{\text{eutec}} = 0.14$ ($\text{Li}_{1.14}\text{Mn}_{0.58}\text{Ti}_{0.28}\text{O}_2$). The experimental DRX phase boundary in this composition range is also linearly sloped, though the decrease of T_{disord} within experiment is less pronounced compared to the simulations. The experimental eutectoid point is projected to be near the temperature $T_{\text{eutec, exp}} = 680^\circ\text{C}$ and composition $x_{\text{eutec, exp}} \sim 0.2 - 0.25$ ($\text{Li}_{1.2}\text{Mn}_{0.4}\text{Ti}_{0.4}\text{O}_2$ to $\text{Li}_{1.25}\text{Mn}_{0.25}\text{Ti}_{0.5}\text{O}_2$). Thus, the experimental and calculated eutectoid temperatures are in reasonable agreement, while the experimental eutectoid composition is significantly higher in Li and Ti concentration than the calculated value. Adding more Li and Ti past x_{eutec} leads to a linear increase in the calculated T_{disord} until the Li_2TiO_3 end-point (Figure 6.3a). The experiments show an increase in T_{disord} at $x > x_{\text{eutec, exp}}$ as well. Specifically, the experimentally measured T_{disord} of $\text{Li}_{1.3}\text{Mn}_{0.1}\text{Ti}_{0.6}\text{O}_2$ is 60°C higher than that of $\text{Li}_{1.25}\text{Mn}_{0.25}\text{Ti}_{0.5}\text{O}_2$. The increase of T_{disord} at high Ti content is consistent with the fact that the reported T_{disord} values of Li_2TiO_3 range from $1155 - 1200^\circ\text{C}$ [251, 252], which is higher than our experimentally obtained $T_{\text{eutec, exp}}$ (680°C).

To understand the differences in phase stability when Ti^{4+} is replaced with Mn^{4+} , we examine the $\text{Li}_{1+x}\text{Mn}_{1-3x}^{3+}\text{Mn}_{2x}^{4+}\text{O}_2$ pseudo-binary, as shown in Figure 6.3b. The trends predicted by theory near the LiMnO_2 composition, specifically within the composition range $0 < x < 0.1$, are similar to those observed for $\text{Li}_{1+x}\text{Mn}_{1-3x}^{3+}\text{Ti}_{2x}^{4+}\text{O}_2$ (Figure 6.3a) in which T_{disord} decreases as a function of x . The predicted eutectoid point of $\text{Li}_{1+x}\text{Mn}_{1-3x}^{3+}\text{Mn}_{2x}^{4+}\text{O}_2$ is at $T_{\text{eutec}} = 970^\circ\text{C}$ and $x_{\text{eutec}} = 0.08$ ($\text{Li}_{1.08}\text{Mn}_{0.92}\text{O}_2$ or $\text{Li}_{1.08}\text{Mn}_{0.76}^{3+}\text{Mn}_{0.16}^{4+}\text{O}_2$ – Figure 6.3b), which is at significantly higher T_{eutec} and lower x_{eutec} than for the Ti^{4+} system. At $x > 0.08$, the T_{disord} rapidly increases as a function of x , leading to a prominent DRX – lay-

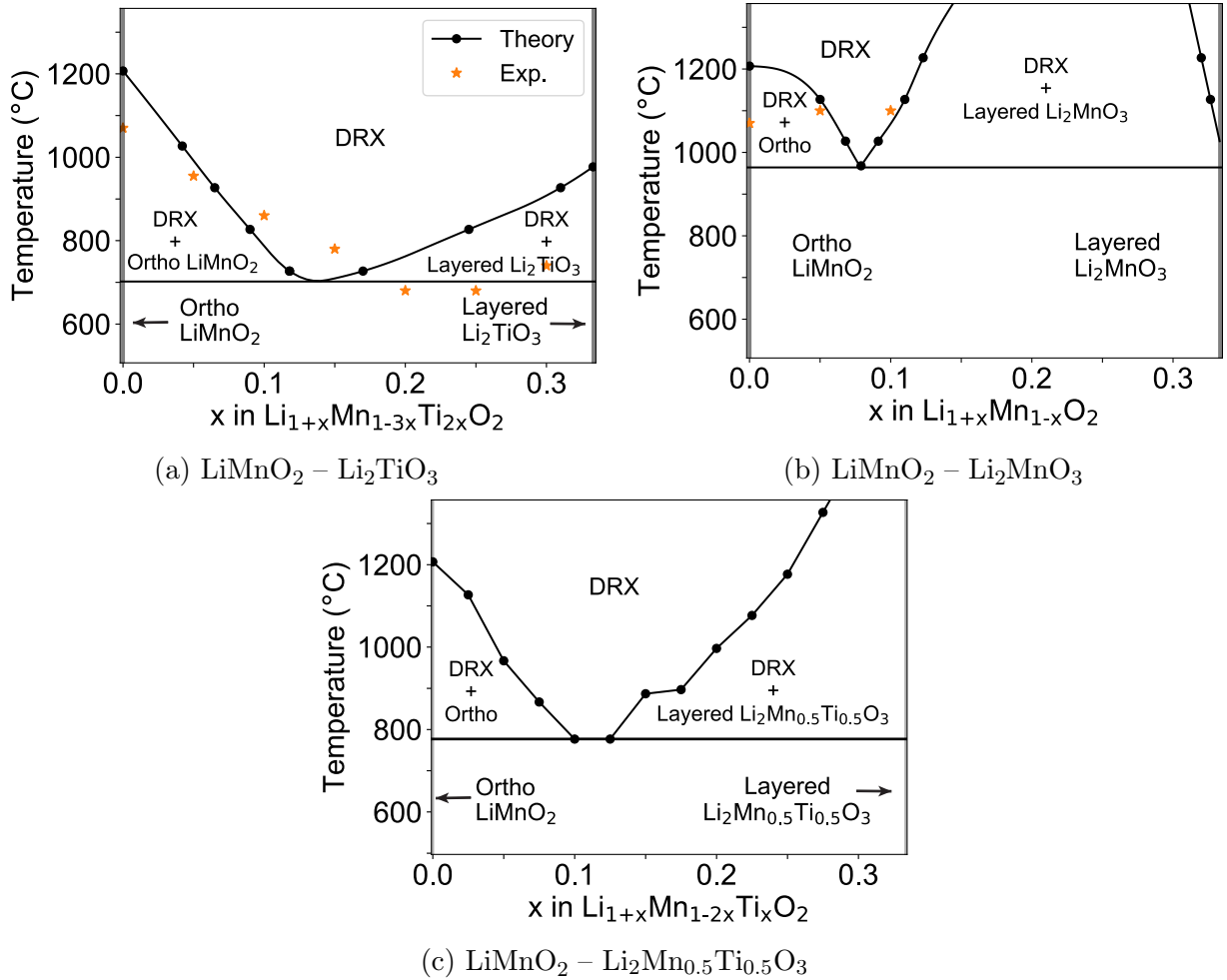


Figure 6.3: Temperature – composition phase diagrams of the pseudo-binary composition spaces of a) $\text{LiMnO}_2 - \text{Li}_2\text{TiO}_3$, b) $\text{LiMnO}_2 - \text{Li}_2\text{MnO}_3$, and c) $\text{LiMnO}_2 - \text{Li}_2\text{Mn}_{0.5}\text{Ti}_{0.5}\text{O}_3$, calculated from MC simulations (black lines). Gold stars represent T_{disord} determined from *in situ* XRD experiments, which were performed for select compositions along the $\text{LiMnO}_2 - \text{Li}_2\text{TiO}_3$ and $\text{LiMnO}_2 - \text{Li}_2\text{MnO}_3$ pseudo-binaries only.

ered Li_2MnO_3 two-phase region. The dominant factor leading to this wider two-phase region is the high predicted T_{disord} of Li_2MnO_3 ($> 2800^\circ\text{C}$), which is significantly higher than the simulated T_{disord} of Li_2TiO_3 (1000°C). Thus, the layered Li_2MnO_3 phase is predicted to be very stable and competes strongly with DRX at typical DRX synthesis temperature ranges ($\sim 1000^\circ\text{C}$), significantly reducing the range of $\text{Li}_{1+x}\text{Mn}_{1-3x}^{3+}\text{Mn}_{2x}^{4+}\text{O}_2$ DRX compositions that are accessible at reasonable temperatures.

Our experimentally determined T_{disord} of $\text{Li}_{1.05}\text{Mn}_{0.95}\text{O}_2$ and $\text{Li}_{1.1}\text{Mn}_{0.9}\text{O}_2$ are nearly iden-

tical at 1100 °C, which are in excellent agreement (within ± 50 °C) with the computed DRX phase boundary (Figure 6.3b). We have performed *in situ* XRD experiments at higher Li and Mn^{4+} concentration, specifically at $x = 0.15, 0.2, 0.25$, and 0.3 , from which we could not determine T_{disord} because the temperature at which DRX becomes phase-pure could not be reached due to our furnace’s maximum temperature of 1100 °C, indicating that the T_{disord} is greater than this temperature, which is consistent with Figure 6.3b. Thus, although we could not experimentally quantify T_{disord} at these compositions, we confirm that these T_{disord} are very high and thus validate our prediction of a wide DRX – layered Li_2MnO_3 miscibility gap.

To understand the effect of combining Mn^{4+} and Ti^{4+} on phase stability, we calculate the pseudo-binary phase diagram between LiMnO_2 – $\text{Li}_2\text{Mn}_{0.5}\text{Ti}_{0.5}\text{O}_3$ which contains an equal fraction of Mn^{4+} and Ti^{4+} ($\text{Li}_{1+x}\text{Mn}_{1-3x}^{3+}\text{Mn}_x^{4+}\text{Ti}_x^{4+}\text{O}_2$), and is shown in Figure 6.3c. Within $\text{Li}_{1+x}\text{Mn}_{1-3x}^{3+}\text{Mn}_x^{4+}\text{Ti}_x^{4+}\text{O}_2$, there is a rapid decrease in T_{disord} at low x until the eutectoid point of $T_{\text{eutec}} \sim 770$ °C and $x_{\text{eutec}} \sim 0.11$ ($\text{Li}_{1.11}\text{Mn}_{0.78}\text{Ti}_{0.11}\text{O}_2$), which is comparable to the eutectoid point in the $\text{Li}_{1+x}\text{Mn}_{1-3x}^{3+}\text{Ti}_{2x}^{4+}\text{O}_2$ system (Figure 6.3a). In fact, the DRX phase boundary in the region of $x < 0.11$ is nearly identical to the $\text{Li}_{1+x}\text{Mn}_{1-3x}^{3+}\text{Ti}_{2x}^{4+}\text{O}_2$ system (Figure 6.3a), which is consistent with a purely entropy-driven increase in the stability of the DRX phase. At higher x , there is a prominent two-phase region between DRX and layered $\text{Li}_2\text{Mn}_{0.5}\text{Ti}_{0.5}\text{O}_3$, though this region is significantly smaller than the miscibility gap between DRX and layered Li_2MnO_3 (shown in Figure 6.3b). Thus, the partial substitution of Mn^{4+} with Ti^{4+} increases the accessible composition range of DRX at $900 < T < 1200$ °C. We predict the T_{disord} of $\text{Li}_2\text{Mn}_{0.5}\text{Ti}_{0.5}\text{O}_3$ to be quite high (~ 1900 °C), which rationalizes why the two-phase region between DRX and layered $\text{Li}_2\text{Mn}_{0.5}\text{Ti}_{0.5}\text{O}_3$ is still relatively large. An important contribution to the stability of layered $\text{Li}_2\text{Mn}_{0.5}\text{Ti}_{0.5}\text{O}_3$ is the configurational entropy (S_{config}) of mixing Mn^{4+} and Ti^{4+} within this phase, which significantly lowers the free energy (Appendix Figure 6.12). Meanwhile, the S_{config} in layered Li_2MnO_3 and Li_2TiO_3 is found to be negligible up to their transition temperature, since they exhibit a first-order transition to the disordered state (Appendix Figure 6.13).

To experimentally investigate the miscibility regions of the LMTO phase diagram, we perform *ex situ* XRD characterization of several samples quenched from above and below the respective T_{disord} . Through this analysis, we also assess the practical feasibility of quenching phase-pure DRX samples near the identified T_{disord} . The *ex situ* XRD patterns of quenched $\text{Li}_{1.05}\text{Mn}_{0.85}\text{Ti}_{0.1}\text{O}_2$, $\text{Li}_{1.1}\text{Mn}_{0.7}\text{Ti}_{0.2}\text{O}_2$, $\text{Li}_{1.25}\text{Mn}_{0.25}\text{Ti}_{0.5}\text{O}_2$, and $\text{Li}_{1.3}\text{Mn}_{0.1}\text{Ti}_{0.6}\text{O}_2$ samples are shown in Figure 6.4. For the $\text{Li}_{1.05}\text{Mn}_{0.85}\text{Ti}_{0.1}\text{O}_2$ (Figure 6.4a) and $\text{Li}_{1.1}\text{Mn}_{0.7}\text{Ti}_{0.2}\text{O}_2$ (Figure 6.4b) compositions, the XRD patterns of samples quenched from 1000 °C and 900 °C, respectively, display only the peaks of a DRX reference, which confirms that phase-pure DRX can be isolated slightly above T_{disord} . Refinement results show that the DRX lattice parameters are 4.17 Å and 4.16 Å for $\text{Li}_{1.05}\text{Mn}_{0.85}\text{Ti}_{0.1}\text{O}_2$ and $\text{Li}_{1.1}\text{Mn}_{0.7}\text{Ti}_{0.2}\text{O}_2$ (Appendix Figure 6.14), respectively, which are in agreement with previously reported results from typical solid-state synthesis methods [240]. When these samples are quenched from a temperature

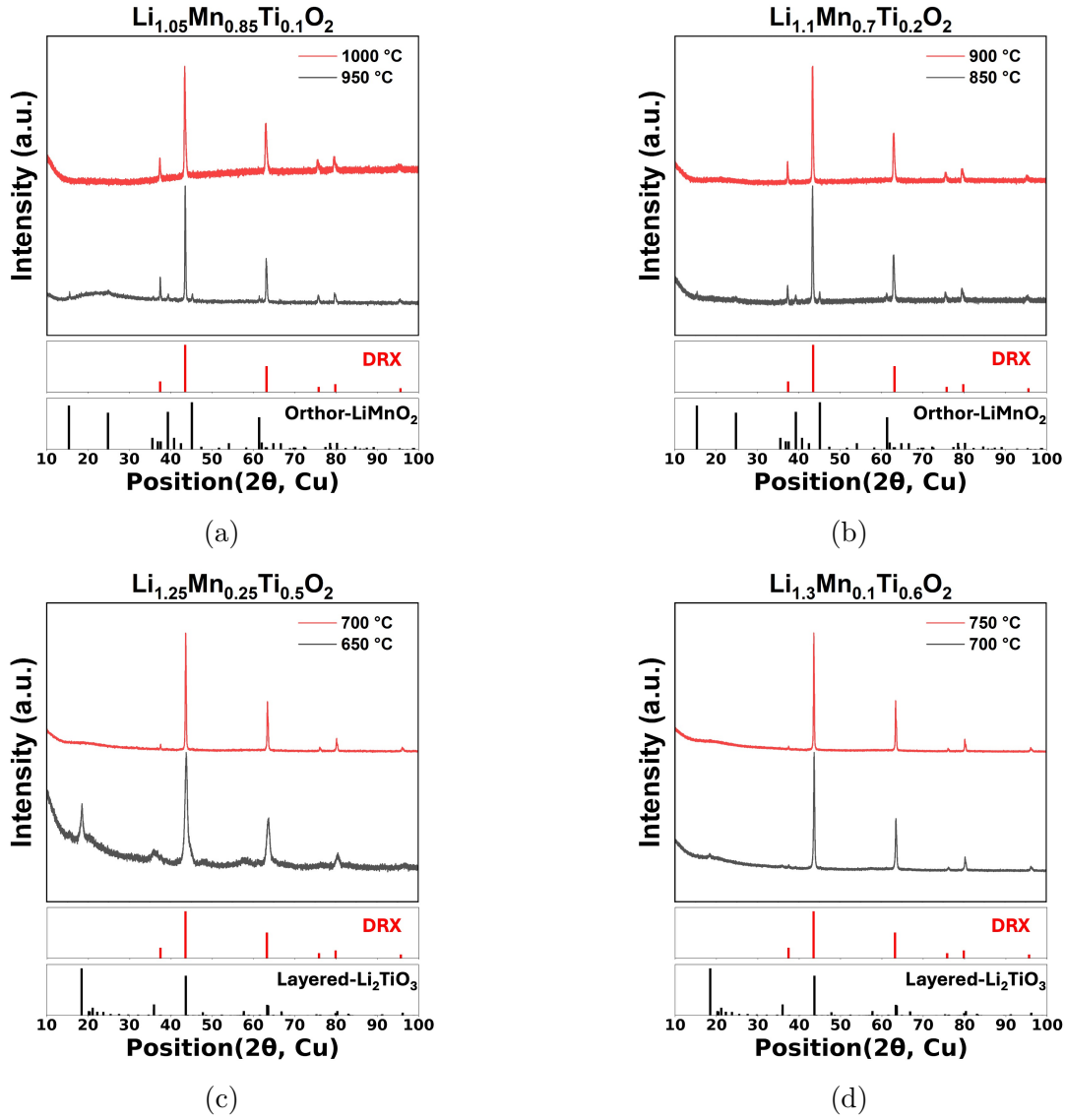


Figure 6.4: *Ex situ* XRD patterns of samples quenched from various temperatures. a) $\text{Li}_{1.05}\text{Mn}_{0.85}\text{Ti}_{0.1}\text{O}_2$, b) $\text{Li}_{1.1}\text{Mn}_{0.7}\text{Ti}_{0.2}\text{O}_2$, c) $\text{Li}_{1.25}\text{Mn}_{0.25}\text{Ti}_{0.5}\text{O}_2$, and d) $\text{Li}_{1.3}\text{Mn}_{0.1}\text{Ti}_{0.6}\text{O}_2$, each quenched from temperatures above (red) and below (black) their respective T_{disord} .

slightly below T_{disord} , the XRD pattern contains small impurity peaks that can be ascribed to orthorhombic LiMnO_2 , in addition to the majority DRX peaks (Figures 6.4a and 6.4b). The presence of a two-phase mixture of DRX and orthorhombic LiMnO_2 validates that the samples quenched from below T_{disord} are in the two-phase coexistence region, as predicted by our first-principles phase diagram of $\text{Li}_{1+x}\text{Mn}_{1-3x}^{3+}\text{Ti}_{2x}^{4+}\text{O}_2$ (Figure 6.3a). Similarly, for the more Li and Ti-rich compositions, $\text{Li}_{1.25}\text{Mn}_{0.25}\text{Ti}_{0.5}\text{O}_2$ (Figure 6.4c) and $\text{Li}_{1.3}\text{Mn}_{0.1}\text{Ti}_{0.6}\text{O}_2$

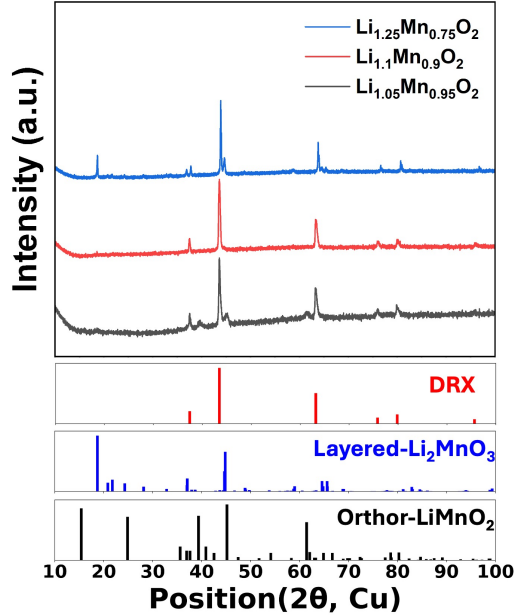


Figure 6.5: *Ex situ* XRD patterns of compositions $\text{Li}_{1.05}\text{Mn}_{0.95}\text{O}_2$, $\text{Li}_{1.1}\text{Mn}_{0.9}\text{O}_2$, and $\text{Li}_{1.25}\text{Mn}_{0.75}\text{O}_2$, each quenched from 1100 °C.

(Figure 6.4d), which are past the eutectic point, pure DRX can be obtained above T_{disord} while layered Li_2TiO_3 is found to coexist with DRX below T_{disord} . The lattice parameters of the pure $\text{Li}_{1.25}\text{Mn}_{0.25}\text{Ti}_{0.5}\text{O}_2$ and $\text{Li}_{1.3}\text{Mn}_{0.1}\text{Ti}_{0.6}\text{O}_2$ DRX phases are refined to be 4.14 Å and 4.13 Å, respectively (Appendix Figure 6.15).

Replacing Ti^{4+} with Mn^{4+} leads to markedly different phase behavior. *Ex situ* XRD patterns of $\text{Li}_{1.05}\text{Mn}_{0.95}\text{O}_2$, $\text{Li}_{1.1}\text{Mn}_{0.9}\text{O}_2$, and $\text{Li}_{1.25}\text{Mn}_{0.75}\text{O}_2$ samples, quenched from 1100 °C are shown in Figure 6.5. Upon quenching $\text{Li}_{1.05}\text{Mn}_{0.95}\text{O}_2$, the resulting sample is predominantly a DRX phase with minor orthorhombic impurities (Figure 6.5). This observation is surprising because our *in situ* XRD patterns show that DRX is phase pure at ~ 1100 °C (Appendix Figure 6.16). We therefore attribute the presence of the orthorhombic impurity to the quench being too slow. As a result, the quenched samples may reflect the equilibrium phase behavior at lower temperatures, where $\text{Li}_{1.05}\text{Mn}_{0.95}\text{O}_2$ would lie within a predicted two-phase region between orthorhombic LiMnO_2 and DRX (Figure 6.3b). A reduced fraction of the orthorhombic phase is observed for $\text{Li}_{1.1}\text{Mn}_{0.9}\text{O}_2$, with DRX remaining the dominant phase, as indicated by the red XRD pattern in Figure 6.5. In contrast, quenching $\text{Li}_{1.25}\text{Mn}_{0.75}\text{O}_2$ from 1100 °C yields a mixture of layered Li_2MnO_3 and DRX, in agreement with the corresponding two-phase region in the computed phase diagram (Figure 6.3b).

When quenching $\text{Li}_{1.05}\text{Mn}_{0.95}\text{O}_2$ from a slightly lower temperature of 1000 °C, we identify a third phase in addition to orthorhombic LiMnO_2 and DRX. The corresponding XRD pattern is shown in Appendix Figure 6.17 and we assign this additional phase to be layered LiMnO_2 , with possible Li-excess. Since lithiated spinel and layered LiMnO_2 have similar XRD patterns, we performed further first-principles calculations to analyze the stability of these phases.

6.3 Phase stability and structural distortions within Li-excess phases

To rationalize the experimentally observed (meta)stability of the Li-excess layered phase from first principles, we compare the DFT-computed energies of the layered, orthorhombic, and spinel phases at the $\text{Li}_{1.0625}\text{Mn}_{0.9375}\text{O}_2$ ($\text{Li}_{1.0625}\text{Mn}_{0.8125}^{3+}\text{Mn}_{0.125}^{4+}\text{O}_2$) composition. Because these phases need to accommodate Li-excess through partial occupancy of the Mn sites, we enumerate symmetrically distinct configurations of each phase and compute the energies above the hull (E_{hull}), which are shown in Figure 6.6a. Though all structures have positive values of $E_{\text{hull}} \geq 17$ meV/atom, the layered configurations are lower ($E_{\text{hull}} \approx 17$ meV/atom) than the orthorhombic and spinel configurations ($E_{\text{hull}} \geq 19$ meV/atom). The favorability of the Li-excess layered phase suggests that the experimentally found impurity phase in Appendix Figure 6.17 is indeed a Li-excess layered phase, which forms as a metastable phase at that composition when phase separation cannot occur fast enough. This trend clearly contrasts with the stoichiometric LiMnO_2 composition, in which the orthorhombic phase is the ground state (Appendix Figure 6.18). We note that these sets of enumerated Li-excess structures are not exhaustive, so there may be other possible orderings of each phase that are not considered.

To rationalize the impact of Ti doping on the phase stability, we similarly calculate E_{hull} of the orthorhombic, layered, and spinel phases at the $\text{Li}_{1.0625}\text{Mn}_{0.8125}\text{Ti}_{0.125}\text{O}_2$ composition, which is plotted in Figure 6.6b. These structures also have energies above the convex hulls with $E_{\text{hull}} \geq 12$ meV/atom, though these values are on average lower than the $\text{Li}_{1.0625}\text{Mn}_{0.9375}\text{O}_2$ structures (Figure 6.6a). For the $\text{Li}_{1.0625}\text{Mn}_{0.8125}\text{Ti}_{0.125}\text{O}_2$ composition, the orthorhombic phase is the more energetically favorable as it contains the lowest energy orderings, followed by the layered and spinel phases (Figure 6.6b).

These phase stability trends of Li-excess phases are relatively consistent when the Li content increases. The computed E_{hull} of these phases at the $\text{Li}_{1.125}\text{Mn}_{0.875}\text{O}_2$ and $\text{Li}_{1.125}\text{Mn}_{0.625}\text{Ti}_{0.25}\text{O}_2$ compositions are shown in Figures 6.6c and 6.6d. All configurations are predicted to have energies above the hull. For the $\text{Li}_{1.125}\text{Mn}_{0.875}\text{O}_2$ phases, we find that layered and spinel have the lowest energy configurations. In the Ti-doped $\text{Li}_{1.125}\text{Mn}_{0.625}\text{Ti}_{0.25}\text{O}_2$ composition, the orthorhombic phase contains the most energetically favorable configurations.

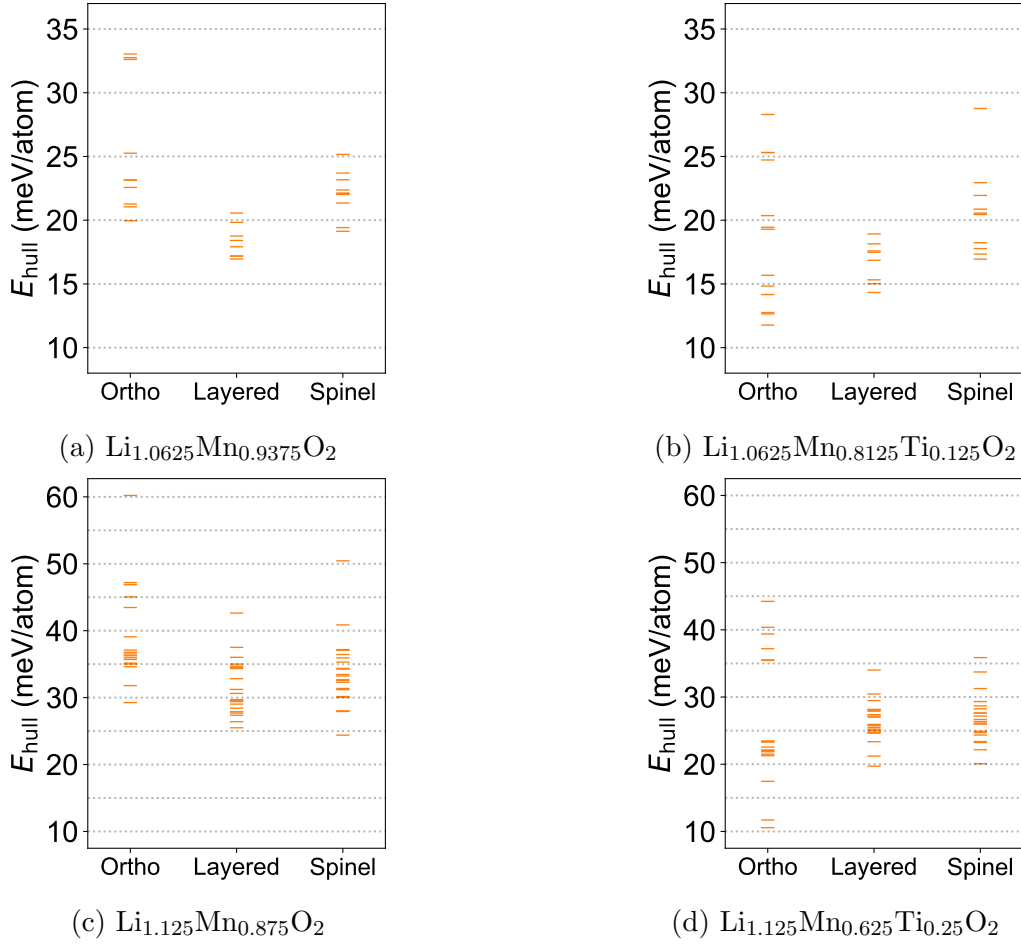


Figure 6.6: Energy above the hull (E_{hull}) of Li-excess orthorhombic (ortho), layered, spinel, and γ phases at the a) $\text{Li}_{1.0625}\text{Mn}_{0.9375}\text{O}_2$ and b) $\text{Li}_{1.0625}\text{Mn}_{0.8125}\text{Ti}_{0.125}\text{O}_2$, c) $\text{Li}_{1.125}\text{Mn}_{0.875}\text{O}_2$, and d) $\text{Li}_{1.125}\text{Mn}_{0.625}\text{Ti}_{0.25}\text{O}_2$ compositions, computed from DFT at $T = 0$ K.

These computed energies suggest that for Li-excess compositions along $\text{Li}_{1+x}\text{Mn}_{1-3x}^{3+}\text{Mn}_{2x}^{4+}\text{O}_2$, the layered phase is metastable against phase separation but more energetically favorable compared to the orthorhombic phase. Since these computed energies do not include entropic effects, we perform additional canonical MC simulations to calculate the free energy of the Li-excess layered phase at temperatures up to 800 °C, but find that the free energy always lies above the convex hull (Appendix Figure 6.19). The predicted metastability of the layered phase suggests that the layered phases observed in experiment (Appendix Figure 6.17) are kinetically trapped metastable phases. Upon doping with Ti^{4+} , the Li-excess layered phase is not found in $\text{Li}_{1+x}\text{Mn}_{1-3x}^{3+}\text{Ti}_{2x}^{4+}\text{O}_2$ possibly because the orthorhombic phase is more energetically favorable compared to the layered phase within this composition range.

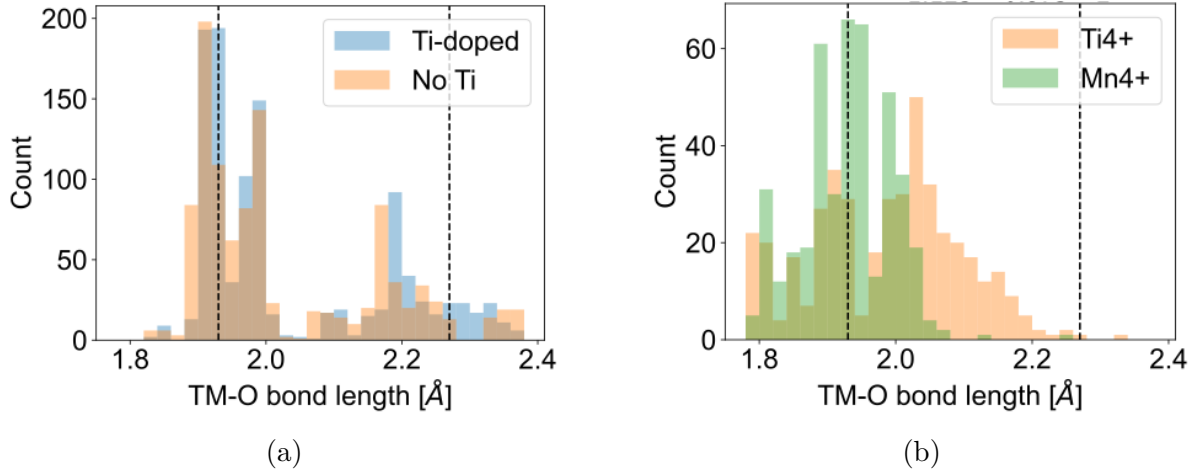


Figure 6.7: Histograms of TM–O bond lengths in Li-excess ortho $\text{Li}_{1.125}\text{Mn}_{0.875}\text{O}_2$ and Ti-doped $\text{Li}_{1.125}\text{Mn}_{0.625}\text{Ti}_{0.25}\text{O}_2$ structures. a) Mn^{3+} -O bond lengths within structures containing Ti-doping and no Ti, b) Ti^{4+} -O and Mn^{4+} -O bond lengths. Dashed lines mark the Mn^{3+} -O bond lengths within ortho LiMnO_2 .

To investigate why the orthorhombic Li-excess phase becomes favored upon Ti doping while layered is favored without Ti, we examine the TM–O bond length distributions within the orthorhombic $\text{Li}_{1.125}\text{Mn}_{0.875}\text{O}_2$ and $\text{Li}_{1.125}\text{Mn}_{0.625}\text{Ti}_{0.25}\text{O}_2$ structures. The distributions of Mn^{3+} -O bond lengths are shown in Figure 6.7a. Within both considered compositions, we observe a bimodal distribution of Mn^{3+} -O lengths, arising from the JT distortion of Mn^{3+} . The shorter Mn^{3+} -O bonds are on average ~ 1.92 Å, which is roughly equivalent to the short Mn^{3+} -O bonds in ortho LiMnO_2 (dashed line in Figure 6.7a). The long Mn^{3+} -O bonds are on average ~ 2.2 Å, which are significantly shorter than the long Mn^{3+} -O bonds in ortho LiMnO_2 (2.28 Å). Notably, the long Mn^{3+} -O bond lengths of Ti-doped $\text{Li}_{1.125}\text{Mn}_{0.625}\text{Ti}_{0.25}\text{O}_2$ are slightly but noticeably higher than in $\text{Li}_{1.125}\text{Mn}_{0.875}\text{O}_2$, reflecting a larger magnitude of JT distortions, which may contribute to the greater stability of the orthorhombic phase in Ti-doped compositions. However, the JT distortions in both Li-excess compositions are clearly suppressed relative to stoichiometric ortho LiMnO_2 .

Furthermore, we examine the distributions of Ti^{4+} -O bonds in $\text{Li}_{1.125}\text{Mn}_{0.625}\text{Ti}_{0.25}\text{O}_2$ and Mn^{4+} -O bonds in $\text{Li}_{1.125}\text{Mn}_{0.875}\text{O}_2$ in Figure 6.7b. The average Ti^{4+} -O bond lengths are ~ 2 Å, with a relatively large spread of values between 1.8 – 2.2 Å. The Mn^{4+} -O bonds are significantly shorter with an average of ~ 1.92 Å, with only very few Mn^{4+} -O bonds > 2.1 Å. Thus, Ti^{4+} can distort within the octahedral sites to a significantly greater degree than Mn^{4+} , which potentially helps Ti^{4+} accommodate the lattice strains generated by neighboring Mn^{3+} JT distortions. However, the Ti^{4+} -O distribution does not resemble that of the Mn^{3+} -O distributions (Figure 6.7a), suggesting that the Ti^{4+} distort in a different way.

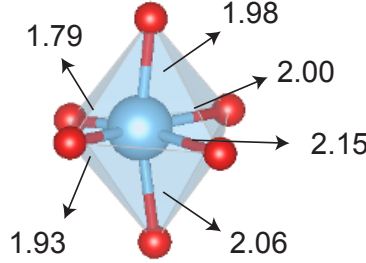


Figure 6.8: TiO_6 octahedron in a relaxed ortho $\text{Li}_{1.125}\text{Mn}_{0.625}\text{Ti}_{0.25}\text{O}_2$ structure with labeled bond lengths in Å.

To clarify the nature of Ti^{4+} distortions, we visualize a TiO_6 octahedron within the lowest energy ortho $\text{Li}_{1.125}\text{Mn}_{0.625}\text{Ti}_{0.25}\text{O}_2$ configuration (relaxed within DFT) in Figure 6.8 with labeled bond lengths. The other TiO_6 octahedra in ortho $\text{Li}_{1.125}\text{Mn}_{0.625}\text{Ti}_{0.25}\text{O}_2$ configurations also resemble the complex shown in Figure 6.8, which contains three relatively longer bond lengths ≥ 2 Å, with the remaining bonds span 1.79 – 1.98 Å. The three longer Ti–O bonds are roughly perpendicular to each other, which is different from a typical Mn^{3+} JT distortion in which two opposing axial Mn–O bonds are elongated, while the four equatorial bonds are shortened. The observed Ti^{4+} distortions more closely resemble those within the ferroelectric rhombohedral $R3m$ BaTiO_3 phase, which arise from the spontaneous polarization [261, 142]. Although these Ti^{4+} distortions are not JT distortions, it is possible that they still help accommodate the lattice strains stemming from neighboring Mn^{3+} JT distortions better than Mn^{4+} , which would rationalize the increased stability of the Li-excess orthorhombic phase upon doping with Ti (Figure 6.6).

6.4 Discussion

Through a combined first-principles and experimental approach, we have mapped the phase diagram of the LMTO rock-salt phases. We have closely analyzed the $\text{Li}_{1+x}\text{Mn}_{1-3x}^{3+}\text{Ti}_{2x}^{4+}\text{O}_2$ ($\text{LiMnO}_2 - \text{Li}_2\text{TiO}_3$), $\text{Li}_{1+x}\text{Mn}_{1-3x}^{3+}\text{Mn}_{2x}^{4+}\text{O}_2$ ($\text{LiMnO}_2 - \text{Li}_2\text{MnO}_3$), and $\text{Li}_{1+x}\text{Mn}_{1-3x}^{3+}\text{Mn}_x^{4+}\text{Ti}_x^{4+}\text{O}_2$ ($\text{LiMnO}_2 - \text{Li}_2\text{Mn}_{0.5}\text{Ti}_{0.5}\text{O}_3$) pseudo-binary phase diagrams (Figure 6.3), each of which are eutectoid-like, in which the order-disorder transition temperature (T_{disord}) varies as off-stoichiometry is introduced to the end-point compositions (adding excess Li to LiMnO_2 or Li deficiency to $\text{Li}_2D^{4+}\text{O}_3$, where D can be Mn, Ti, or an admixture of both). The strong dependence of T_{disord} on composition reveals that the optimization of DRX composition and synthesis temperature are intrinsically coupled. Through heating and *in situ* XRD experiments in an inert atmosphere, we determine the T_{disord} of specific LMTO compositions, which agree reasonably well with the calculated values, though they can deviate by up to ~ 200 °C.

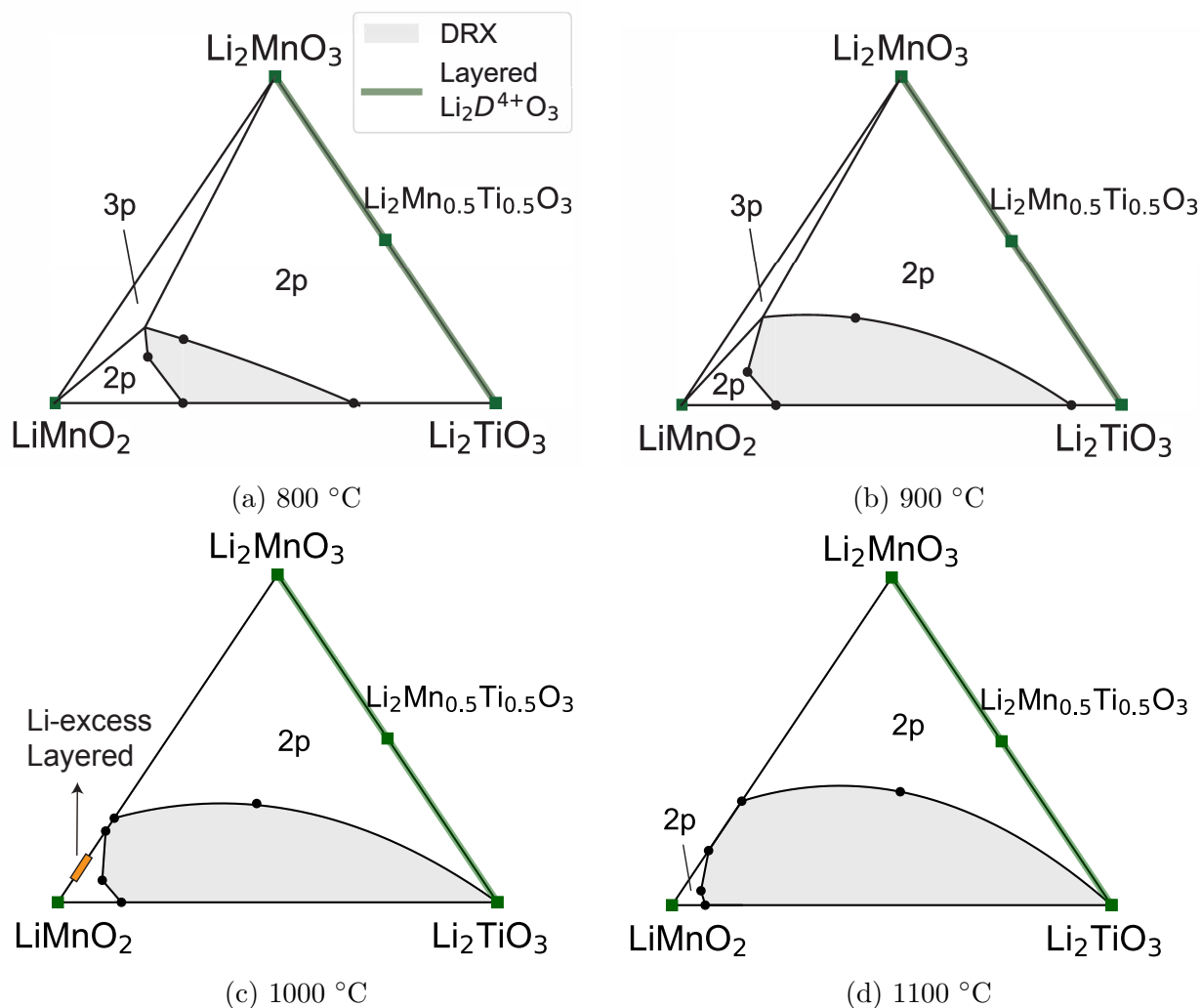


Figure 6.9: Pseudo-ternary phase diagram of LiMnO_2 – Li_2MnO_3 – Li_2TiO_3 at 800, 900, 1000, and 1100 °C. The two-phase and three-phase regions are labeled as 2p and 3p, respectively. Black points are obtained from the calculated pseudo-binary phase diagrams (Figure 6.3) and the lines are interpolations between them. Gray shaded regions are DRX, green lines represent layered $\text{Li}_2\text{D}^{4+}\text{O}_3$, and the orange line in c) denotes the Li-excess layered phase observed in experiment, which our calculations predict to be metastable.

We interpolate the calculated pseudo-binary phase diagrams to present a pseudo-ternary phase diagram in Figure 6.9 at temperatures ranging from 800 to 1100 °C, which spans temperatures below and above conventional DRX synthesis temperatures (~ 1000 °C). Our simulations suggest that DRX competes with two other phases, which are orthorhombic LiMnO_2 and layered $\text{Li}_2\text{D}^{4+}\text{O}_3$, at the temperatures considered (800 – 1300 °C). The layered $\text{Li}_2\text{D}^{4+}\text{O}_3$ phase forms a full solid-solution between Li_2MnO_3 and Li_2TiO_3 (Appendix

Figure 6.21). In experiments, quenched samples of certain compositions contain layered LiMnO_2 -like impurity phases as well (Appendix Figure 6.17), which our calculations suggest to be metastable when phase separation does not occur. At 800 °C, DRX is predicted to be stable only in a small range of compositions with moderate concentration of Li-excess and Ti^{4+} (grey shaded regions in Figure 6.9), while the other compositions lie within a miscibility region (unshaded areas). By 900 °C, the composition range of DRX increases significantly, especially in the Ti^{4+} -rich regions (near the $\text{LiMnO}_2 - \text{Li}_2\text{TiO}_3$ pseudo-binary). As temperature increases to 1100 °C, DRX is stable within nearly the entire $\text{LiMnO}_2 - \text{Li}_2\text{TiO}_3$ composition space, except in the regions with very little Li-excess, while it is only stable within a limited region within $\text{LiMnO}_2 - \text{Li}_2\text{MnO}_3$. Thus, there is an increasing width of the miscibility gap between DRX and $\text{Li}_2\text{D}^{4+}\text{O}_3$ as the ratio of Mn^{4+} to Ti^{4+} increases. These trends are verified by our experimental determination of T_{disord} along $\text{Li}_{1+x}\text{Mn}_{1-3x}^{3+}\text{Ti}_{2x}^{4+}\text{O}_2$ and $\text{Li}_{1+x}\text{Mn}_{1-3x}^{3+}\text{Mn}_{2x}^{4+}\text{O}_2$ (Figure 6.3).

The distinct impact of Ti^{4+} and Mn^{4+} on the thermodynamic accessibility of DRX can be attributed to the differences in electronic structure. Ti^{4+} has negligible filling of d-shell states (d^0), while Mn^{4+} contains d-shells that are partially filled. It was shown by Urban et al. that, compared to TM species with d-shells that are (partially) filled, ions with the d^0 electronic structure can better stabilize disordered configurations, as the local lattice distortions that are inherently present in disordered configurations can be accommodated with minimal energy cost [247]. These differences in electronic structure rationalize why the T_{disord} tends to increase significantly as the ratio of Mn^{4+} to Ti^{4+} increases. Notably, the layered Li_2MnO_3 structure is predicted from MC simulations to have a remarkably high $T_{\text{disord}} > 2800$ °C — which may not be realistic as this method does not account for potential melting or reduction, which would occur before reaching such a high temperature. Nevertheless, the high predicted T_{disord} reflects the steep energy cost to disorder the layered Li_2MnO_3 structure. Thus, compositions with substantial Mn^{4+} content favor phase separation into layered Li_2MnO_3 (or $\text{Li}_2\text{D}^{4+}\text{O}_3$ with high Mn^{4+} content), substantially limiting the DRX composition range that is accessible at reasonable temperatures. These results rationalize why there have been few reports of d^0 -free and Mn-rich DRX synthesized without the utilization of high-energy mechano-chemical milling techniques [243, 262].

Meanwhile, layered Li_2TiO_3 has a much lower predicted T_{disord} of 1000 °C, reflecting a lower energy cost to disorder. The significantly lower T_{disord} of layered Li_2TiO_3 has pivotal implications, as it implies that the compositions with moderate to high fraction of Ti^{4+} can disorder at much lower temperatures. Specifically, a significant composition range of DRX is stable at temperatures of 800 – 900 °C, suggesting the potential of lowering the synthesis temperature of many DRX compositions below the conventionally used temperatures ≥ 1000 °C [20, 22]. At 900 °C, DRX within the $\text{Li}_{1+x}\text{Mn}_{1-3x}^{3+}\text{Ti}_{2x}^{4+}\text{O}_2$ space is predicted to be stable in the range of Li-excess fraction (x) spanning 0.07 – 0.28, while in $\text{Li}_{1+x}\text{Mn}_{1-3x}^{3+}\text{Mn}_x^{4+}\text{Ti}_x^{4+}\text{O}_2$ it is stable for x spanning 0.07 – 0.14 (Figure 6.3). The accessible composition range of DRX shrinks significantly as the temperature decreases to 800 °C, but an appreciable portion

remains (Figure 6.9). Lowering the synthesis temperature is instrumental towards lowering the synthesis energy cost and the ability to optimize DRX particle size, which is subject to rapid coarsening at high temperature, thereby reducing rate performance [20]. Although we predict and verify from experiments that certain compositions have reasonably low T_{disord} , we find that some samples such as $\text{Li}_{1.05}\text{Mn}_{0.95}\text{O}_2$ quenched from above the identified T_{disord} are not pure DRX (Figure 6.5). This is likely due to the quench not being fast enough to retain the high-temperature state. Thus, it is essential to develop synthesis methods that can rapidly cool samples with precise temperature control, so samples spend minimal time within two-phase regions.

It is important to note that some compositions containing an admixture of Mn^{4+} and Ti^{4+} can also have reasonably low T_{disord} . This is exemplified by our prediction of $T_{\text{disord}} \approx 800$ °C for compositions near $\text{Li}_{1.1}\text{Mn}_{0.7}^{3+}\text{Mn}_{0.1}^{4+}\text{Ti}_{0.1}^{4+}\text{O}_2$ (Figure 6.3c). In fact, the simulated phase boundary of DRX in the $\text{Li}_{1+x}\text{Mn}_{1-3x}^{3+}\text{Mn}_x^{4+}\text{Ti}_x^{4+}\text{O}_2$ phase diagram (Figure 6.3c) is nearly identical to the one in $\text{Li}_{1+x}\text{Mn}_{1-3x}^{3+}\text{Ti}_{2x}^{4+}\text{O}_2$ (Figure 6.3a) at relatively small fractions of Li-excess ($x \leq 0.1$). To our knowledge, these compositions containing both Ti^{4+} and Mn^{4+} have not been previously reported, and thus constitute a relatively new design space in which LMTO DRX can be explored and optimized. The (partial) substitution of Ti^{4+} with Mn^{4+} is potentially important as Wu et al. have recently shown that Mn-rich DRX compositions without Ti can yield higher energy density compared to compositions containing Ti, given the same Li concentration [262]. These observations suggest that an optimal balance between thermodynamic accessibility and electrochemical performance can be found by tuning the fraction of Mn^{4+} and Ti^{4+} , especially near Li fractions ≈ 1.05 to 1.1. Although the full replacement of Ti^{4+} with Mn^{4+} generally yields higher T_{disord} , our calculations predict that the Ti-free DRX composition $\approx \text{Li}_{1.08}\text{Mn}_{0.92}\text{O}_2$ has a relatively accessible $T_{\text{disord}} \sim 1000$ °C, as this is the eutectoid point of $\text{Li}_{1+x}\text{Mn}_{1-3x}^{3+}\text{Mn}_{2x}^{4+}\text{O}_2$.

We note that many previous studies have incorporated fluorine (F) into the anion sublattice of DRX, which could impact the T_{disord} [21]. In a recent study, Liang et al. applied *in situ* XRD to determine the T_{disord} of F-doped $\text{Li}_{1.1}\text{Mn}_{0.8}\text{Ti}_{0.1}\text{O}_{1.9}\text{F}_{0.1}$ to be ~ 1000 °C [260], which is close to our experimentally determined T_{disord} of $\text{Li}_{1.05}\text{Mn}_{0.85}\text{Ti}_{0.1}\text{O}_2$ (~ 960 °C), which contains the same fraction of Ti. Given this close agreement of T_{disord} , we do not expect that the T_{disord} of compositions containing a small fraction of F would deviate far from our results. It should also be noted that one study has questioned whether any significant F incorporation occurs when the Mn content is very high [263].

In general, our first-principles and experimental phase diagram are in reasonable agreement with each other. Specifically, the predicted changes of T_{disord} with composition agree qualitatively with experiment. However, the quantitative agreement is lacking in some regions of the phase diagram, as the simulated T_{disord} can significantly deviate from the experimental values by up to 150 – 200 °C, for example at the LiMnO_2 and Li_2TiO_3 compositions. The predicted T_{disord} tends to be more accurate for intermediate compositions

along $\text{Li}_{1+x}\text{Mn}_{1-3x}^{3+}\text{Ti}_{2x}^{4+}\text{O}_2$ and $\text{Li}_{1+x}\text{Mn}_{1-3x}^{3+}\text{Mn}_{2x}^{4+}\text{O}_2$, as they are typically within 100 °C of the experimental values. For $\text{Li}_{1+x}\text{Mn}_{1-3x}^{3+}\text{Ti}_{2x}^{4+}\text{O}_2$, experiments yield a eutectoid composition $\approx \text{Li}_{1.2}\text{Mn}_{0.4}\text{Ti}_{0.4}\text{O}_2$, which contains higher Li concentration compared to the calculated eutectoid composition ($\text{Li}_{1.14}\text{Mn}_{0.58}\text{Ti}_{0.28}\text{O}_2$), though the predicted eutectoid temperature (700 °C) is in close agreement with experiment (~ 680 °C). In experiments we also find layered LiMnO_2 -like phases, specifically along the $\text{Li}_{1+x}\text{Mn}_{1-3x}^{3+}\text{Mn}_{2x}^{4+}\text{O}_2$ pseudo-binary, that are not predicted to be thermodynamically stable within our simulations.

The methods that we employ capture only configurational excitations, while neglecting the vibrational (S_{vib}) and magnetic (S_{mag}) entropy contributions that are also present in this system, potentially rationalizing the difference between theory and experimental results. It has been previously shown that the S_{vib} and its coupling to configurational degrees of freedom can significantly affect predicted T_{disord} and/or solubility limits within alloys [67, 264]. While not always the case, the incorporation of vibrational entropy often shifts calculated order-disorder transitions down. The coupling between S_{vib} and S_{config} has been modeled for simple binary systems using the CE approach [67], but capturing these effects within our higher dimensional quaternary LMTO system would require far greater computational complexity. Magnetic entropy is also present within the LMTO phases, as the orthorhombic LiMnO_2 and layered Li_2MnO_3 phases are antiferromagnetically ordered below their Néel temperatures (~ 280 and 40 K, respectively [195, 248]), so they are magnetically disordered at the elevated temperatures that we analyze.

Another potential source of error in our predicted phase diagram stems from the DFT method employed to generate the dataset used to train the CE model. The LMTO system contains electronic structure complexities that can be challenging to model from DFT — namely the presence of strongly correlated $3d$ electronic states and JT distortions of Mn^{3+} . In a recent study, we specifically highlighted the challenges of modeling the phase stability of the LiMnO_2 polymorphs within DFT, which motivated our selection of the HSE06 hybrid-GGA functional in this study, despite its relatively high computational cost [259]. Specifically, HSE06 can accurately predict orthorhombic LiMnO_2 to be the ground state, while more commonly used GGA+ U and $r^2\text{SCAN}$ approaches predict a spurious LiMnO_2 ground state [259]. It was also shown that the energy differences between phases is highly sensitive to the DFT method used, which indicates that the predicted T_{disord} could possibly be improved by using even more accurate electronic structure methods.

Another potential contribution to the free energy that we have not yet considered is the presence of Mn^{2+} . It is possible for Mn^{2+} to be present within octahedral environments in the rock-salt framework, given that MnO is a known stable phase [265]. Mn^{2+} can form in the LMTO system from the following disproportionation reaction (Equation 6.1).



To investigate the potential influence of Mn^{2+} , we train an additional 5-component CE model that includes Mn^{2+} as a possible species. To train this model, we augment our DFT training

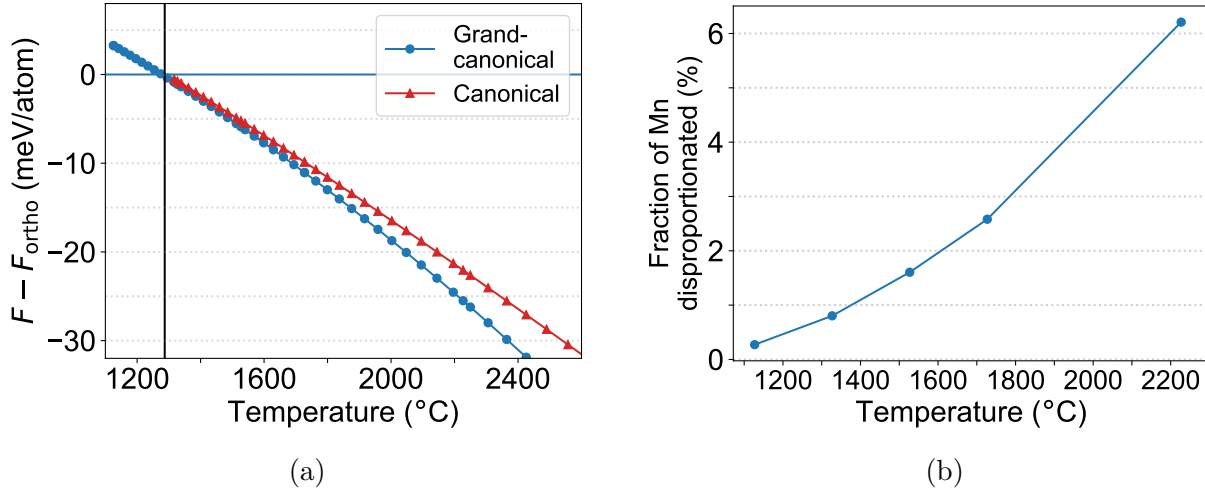


Figure 6.10: Free energies (F) and Mn disproportionation of DRX LiMnO_2 as a function of temperature in MC simulations using a 5-component CE model containing Li^+ , Ti^{4+} , Mn^{2+} , Mn^{3+} , and Mn^{4+} . a) F relative to ortho- LiMnO_2 ($F - F_{\text{ortho}}$) computed within the grand-canonical (GC) and canonical ensembles. GC allows for Mn disproportionation, while canonical maintains Mn in the +3 state only. Vertical line at 1280 $^{\circ}\text{C}$ marks where DRX intersects with ortho- LiMnO_2 , thus the T_{disord} . b) Fraction of Mn disproportionated in DRX LiMnO_2 within GCMC simulations.

structure set to span the $\text{MnO} - \text{Li}_2\text{MnO}_3 - \text{Li}_2\text{TiO}_3$ space (more details in Methods). We calculate the free energy curves of DRX LiMnO_2 from MC simulations within the canonical ensemble containing Mn only in +3 state ($\text{LiMn}^{3+}\text{O}_2$) and charge-neutral GC ensemble (at fixed chemical potentials) that allows for Mn^{3+} disproportionation to form Mn^{2+} and Mn^{4+} as well. These calculated free energies of DRX relative to the orthorhombic LiMnO_2 phase are shown in Figure 6.10a. Within these simulations, the predicted T_{disord} of LiMnO_2 is predicted to be 1280 $^{\circ}\text{C}$, regardless whether Mn disproportionation is accounted for. We track the simulated concentration of Mn^{2+} as a function of temperature in Figure 6.10b, and find that a relatively small fraction of Mn are disproportionated ($< 2\%$) at temperatures below 1600 $^{\circ}\text{C}$. The low fraction of disproportionation events at these elevated temperatures suggests that the energy cost for Mn disproportionation is substantial. Thus, the additional S_{config} of accounting for Mn^{2+} , in addition to Mn^{3+} and Mn^{4+} , is predicted to be minimal at common DRX synthesis temperatures, so we do not expect it to significantly affect the phase boundaries at typical synthesis temperatures.

6.5 Conclusion

A phase diagram of the LMTO rock-salt ($\text{LiMnO}_2 - \text{Li}_2\text{MnO}_3 - \text{Li}_2\text{TiO}_3$) phase space has been derived from first-principles statistical mechanics calculations and XRD experiments. The LMTO phase diagram is identified to be a eutectoid phase diagram, in which the T_{disord} decreases as off-stoichiometry is introduced to the end-point compositions. Importantly, this leads to a significant range of compositions with T_{disord} ranging from 680 – 900 °C, which is much lower than conventional DRX synthesis temperatures (≥ 1000 °C). This finding suggests the potential for lowering synthesis temperature for specific DRX compositions, which can aid in the optimization of particle size/morphology, and in turn the electrochemical performance of LMTO DRX.

6.6 Methods

Theory

All structural enumerations and analysis were performed using the **pymatgen** package [31, 50]. To compute the total energy of each enumerated LMTO rock-salt structure, we perform density-functional theory (DFT) calculations using a plane-wave basis set and the projector augmented wave (PAW) method, as implemented in the Vienna *ab initio* Simulation Package (VASP) [70, 80, 183]. All reported total energies are computed using the HSE06 hybrid generalized gradient approximation (GGA) [113]. Since HSE06 requires significantly higher computational cost than the more commonly utilized GGA and meta-GGA functionals, we calculate the total energy of each structure using HSE06 at the structural geometries optimized at the meta-GGA level (r²SCAN [101]). Specifically, we harness the **atomate2** package [266] to perform a three-step workflow involving the following sequential steps: 1) structural relaxation within GGA (PBEsol+ U [95], where $U = 3.9$ eV) functional, 2) structural relaxation within r²SCAN+ U ($U = 1.8$ eV), and 3) static calculation of the total energy using HSE06, where U are rotationally averaged Hubbard U corrections [106] on Mn-3d electron states that were empirically fitted in previous studies to optimize prediction of Mn oxidation reaction enthalpies [123, 104]. The initial relaxation using PBEsol+ U effectively speeds up the r²SCAN+ U relaxation. Although this approach does not calculate each structure’s true ground state energy within HSE06, we find that the energy differences between select LiMnO_2 phases are reasonably consistent with fully self-consistent HSE06 calculations, with a root mean squared error (RMSE) ~ 1 meV/atom, which is within the error range of the cluster expansion (Appendix Figure 6.18). We estimate that this workflow reduces the computation time by at least a factor of 5 compared to full relaxations using HSE06. More details of the DFT calculations are described in Appendix Note 1.

We use these DFT-computed structures and energies to parametrize a quaternary CE to describe the energies of possible cation orderings of the cubic rock-salt lattice ($\text{Fm}\bar{3}\text{m}$), with a primitive cell lattice parameter $a = 2.97$ Å. The CE represents the total energy of any

configuration as a summation over energy contributions from local cluster interactions [34, 42, 35]. We construct our CE model with pair, triplet, and quadruplet cluster interactions up to cluster distances of 8.91, 5.94, and 5.15 Å, respectively, using the `smol` python package, which is also used for all lattice Monte Carlo (MC) simulations [184]. Mixed ℓ_1 and ℓ_2 norm penalized linear regression (Elastic Net [267]), as implemented in the `scikit-learn` package [268], is used to fit the CE on the DFT energies of 745 unique structures, where the ℓ_1 and ℓ_2 regularization terms promote sparsity and smaller magnitudes of the interactions, respectively. The fit is performed with sample weights applied on the ground state structures and select low-energy structures, a procedure that enables the trained model to correctly preserve the DFT ground states. The 5-fold cross-validation (CV) and training errors of the parametrized CE model are 9.5 meV/atom and 8.5 meV/atom, respectively. The training curves for regularization hyperparameter optimization and further details of CE fitting are shown in Appendix Figure 6.22 and Note 2. The CE predicts the correct energy ordering among the orthorhombic, layered, spinel, and γ LiMnO₂ phases (Appendix Figure 6.18), which further helps validate the model's accuracy. To understand the influence of Mn²⁺, we train an additional CE model that describes a quinary cation site space containing Li⁺, Mn²⁺, Mn³⁺, Mn⁴⁺, and Ti⁴⁺ as possible species. This model was trained in a similar fashion as the quaternary model, with more details described in Appendix Note 2.

Using the quaternary CE model, we perform MC simulations and thermodynamic integration to calculate the free energies of each phase and determine the phase boundaries between them. For the Li_{1+x}Mn_{1-3x}³⁺Ti_{2x}⁴⁺O₂ and Li_{1+x}Mn_{1-3x}³⁺Mn_{2x}⁴⁺O₂ pseudo-binary spaces, we perform charge-neutral grand-canonical (GC)-MC simulations [58] over a range of temperature (T) and chemical potentials (μ), the details of which are described in Appendix Note 2. From these MC trajectories, we perform thermodynamic integration over ensemble-averaged energies and compositions to determine the GC free energy (Ω) of the ortho LiMnO₂, DRX, layered Li₂TiO₃, and layered Li₂MnO₃ phases. The T and μ values where two Ω curves intersect are identified to determine the boundary between the two phases. To calculate Ω , the average GC energy ($\langle\epsilon - \mu N\rangle$) is numerically integrated over inverse thermal energy ($\beta \equiv \frac{1}{k_B T}$) at a fixed reference μ_0 , as described by Equation 6.2 [269]. The μ dependence of Ω is obtained by integrating the average composition ($\langle N \rangle$) over μ at fixed β (Equation 6.3).

$$\beta\Omega(\beta, \mu_0) - \beta_0\Omega(\beta_0, \mu_0) = \int_{\beta_0}^{\beta} \langle\epsilon - \mu_0 N\rangle d\beta, \text{ at fixed } \mu_0 \quad (6.2)$$

$$\Omega(\beta, \mu) - \Omega(\beta, \mu_0) = - \int_{\mu_0}^{\mu} \langle N \rangle d\mu, \text{ at fixed } \beta \quad (6.3)$$

The reference values of μ_0 and β_0 are chosen such that the GC-MC simulations at μ_0 and β_0 equilibrate to the phase of interest. The reference values of β_0 for the ordered phases (ortho LiMnO₂, layered Li₂TiO₃, and layered Li₂MnO₃) are chosen at corresponding T_0 below their

respective T_{disord} . Meanwhile, β_0 of DRX is chosen to be the $T \rightarrow \infty$ limit (equivalently the $\beta \rightarrow 0$ limit), where the free energy can be analytically determined through the expression $\beta_0 \Omega(\beta_0, \mu_0) = -\ln(\sigma)$ [269], where σ is the number of unique arrangements of the LMTO lattice (i.e. $-S_{\text{config}}/k_B$ in the random limit). For a quaternary alloy, this can be trivially evaluated as $\ln(\sigma) = \ln 4$. However, this expression is not valid for the ionic LMTO system, as it accounts for configurations with compositions that are not charge neutral. σ can also be evaluated analytically for a finite supercell of N cation sites and composition defined by n_{Li} , n_{Mn3} , n_{Mn4} , and n_{Ti4} (where n_{Li} is the number of Li, etc) by the expression shown in Equation 6.4a. To facilitate evaluating $\ln(\sigma)$, we apply Stirling's approximation, as shown in Equation 6.4b, which converges quickly with N .

$$\sigma = \frac{N!}{n_{\text{Li}}! n_{\text{Mn3}}! n_{\text{Mn4}}! n_{\text{Ti4}}!} \quad (6.4a)$$

$$\ln(\sigma) \approx N \ln(N) - n_{\text{Li}} \ln(n_{\text{Li}}) - n_{\text{Mn3}} \ln(n_{\text{Mn3}}) - n_{\text{Mn4}} \ln(n_{\text{Mn4}}) - n_{\text{Ti4}} \ln(n_{\text{Ti4}}) \quad (6.4b)$$

σ is thus a function of composition, but in the limits of infinite T and N , the composition will converge to the composition that maximizes S_{config} and in turn σ . Therefore, we perform a GC-MC simulation at $T = 58000$ K and $N = 720$, which converges to an average composition $\approx \text{Li}_{1.2}\text{Mn}_{0.4}^{3+}\text{Mn}_{0.2}^{4+}\text{Ti}_{0.2}^{4+}\text{O}_2$. At this composition, we evaluate using Equation 6.4b $\ln(\sigma) \approx 1.089 k_B/\text{cation}$, which importantly is $\approx 21\%$ lower than the corresponding value for a quaternary alloy ($\ln 4 = 1.386 k_B/\text{cation}$), with the reduction in entropy arising from charge neutrality constraints.

We calculate the $\text{Li}_{1+x}\text{Mn}_{1-3x}^{3+}\text{Mn}_x^{4+}\text{Ti}_x^{4+}\text{O}_2$ pseudo-binary phase diagram using canonical MC simulations and the common tangent construction. The canonical free energy of DRX (F_{DRX}) is computed at compositions x ranging from 0 to 0.3 in increments of 0.025 along $\text{Li}_{1+x}\text{Mn}_{1-3x}^{3+}\text{Mn}_x^{4+}\text{Ti}_x^{4+}\text{O}_2$. The free energy integration scheme to calculate F_{DRX} is identical to the calculation of Ω_{DRX} in the limit of $\mu_0 = 0$ and fixed composition (Equation 6.2). After calculating F , the entropy (S_{config}) can trivially be evaluated as $S_{\text{config}} = \frac{U-F}{T}$.

Experiment

To investigate the disorder temperatures of $\text{Li}_{1+x}\text{Mn}_{1-3x}^{3+}\text{Mn}_{2x}^{4+}\text{O}_2$ ($x=0.05, 0.1, 0.15, 0.2, 0.25, 0.3$), Li_2CO_3 (Sigma, 99%), Mn_2O_3 (Sigma, 99%) and MnO_2 (Alfa Aesar, 99.9%) were used as precursors. For the $\text{Li}_{1+x}\text{Mn}_{1-3x}^{3+}\text{Ti}_{2x}^{4+}\text{O}_2$ series ($x=0.05, 0.1, 0.15, 0.2, 0.25, 0.3$), Li_2CO_3 (Sigma, 99%), Mn_2O_3 (Sigma, 99%) and TiO_2 (Sigma, 99.5%) were used as precursors. For each composition, a total of 4 g of precursors was stoichiometrically mixed in ethanol using a Retsch PM200 planetary ball mill at 250 rpm for 12 h. A 10% excess of Li_2CO_3 was used to compensate for possible lithium loss during high-temperature treatment. The resulting slurry was dried at 70 °C in a convection oven overnight and subsequently ground. Approximately 300 mg of the mixed precursors were pressed into pellets with a diameter of 13 mm.

For *in situ* heating experiments, the pellets were heated to 1100 °C, held at this temperature for 20 min, and then cooled to room temperature using an Anton Paar HTK1200N furnace under a constant nitrogen flow. X-ray diffraction (XRD) data were collected every 10 °C during heating and cooling and continuously collected during holding, using a Bruker D8 Advance diffractometer. All scans were conducted over a 2θ range of 10-70°.

For *ex situ* quenching experiments, pellets were heated to temperatures below and above the respective disorder temperatures and held for 20 min in a tube furnace. The samples were then rapidly removed from the furnace and cooled to room temperature using a fan. A constant argon flow was maintained throughout the heating process. XRD patterns of the quenched samples were collected using an Aeris Minerals diffractometer (Malvern Panalytical) utilizing Cu K α radiation. Scans were performed over a 2θ range of 10-100°.

6.7 Appendix

Note 1: Details of DFT calculations

For each enumerated LMTO structure, we perform a workflow using `atomate2` to optimize the structure and evaluate the total energy. The workflow involves 1) relaxation using PBEsol+ U ($U = 3.9$ eV), 2) relaxation using r²SCAN+ U ($U = 1.8$ eV), then 3) static calculation using HSE06. Steps 2 and 3 use the wave functions and charge density obtained from the previous step as a starting point. The PBEsol+ U relaxations use Li_sv, Mn_pv, Ti_pv, and O PBE PAW pseudopotentials, while the r²SCAN+ U and HSE06 calculations employ an analogous set from the PBE_54 library of PAW within VASP. The energy and force convergence criteria are shown in Table 6.1, which are consistent with the PBE-based MPRelaxSet and r²SCAN-based MPScanRelaxSet settings within `pymatgen`. All calculations use a reciprocal space discretization of $0.25 \text{ \AA}^{-1}$.

Table 6.1: DFT convergence criteria and plane wave energy cutoffs.

Method	Energy conv. (eV)	Force conv. (eV/Å)	Energy cutoff (eV)
PBEsol+ U	$1e-06$	$2e-02$	520
r ² SCAN+ U	$1e-05$	$2e-02$	680
HSE06	$1e-05$	N/A	680

Note 2: Details of CE training and MC simulations

The CE construction and MC simulations are performed using the `smol` package [184]. The CE model is based on a rock-salt lattice with lattice parameter $a = 2.97 \text{ \AA}$. We use an orthonormal sinusoid basis set to represent the pair, triplet, and quadruplet cluster correlation functions up to cluster distances of 8.91, 5.94, and $5.15 \text{ \AA}$, respectively. To describe

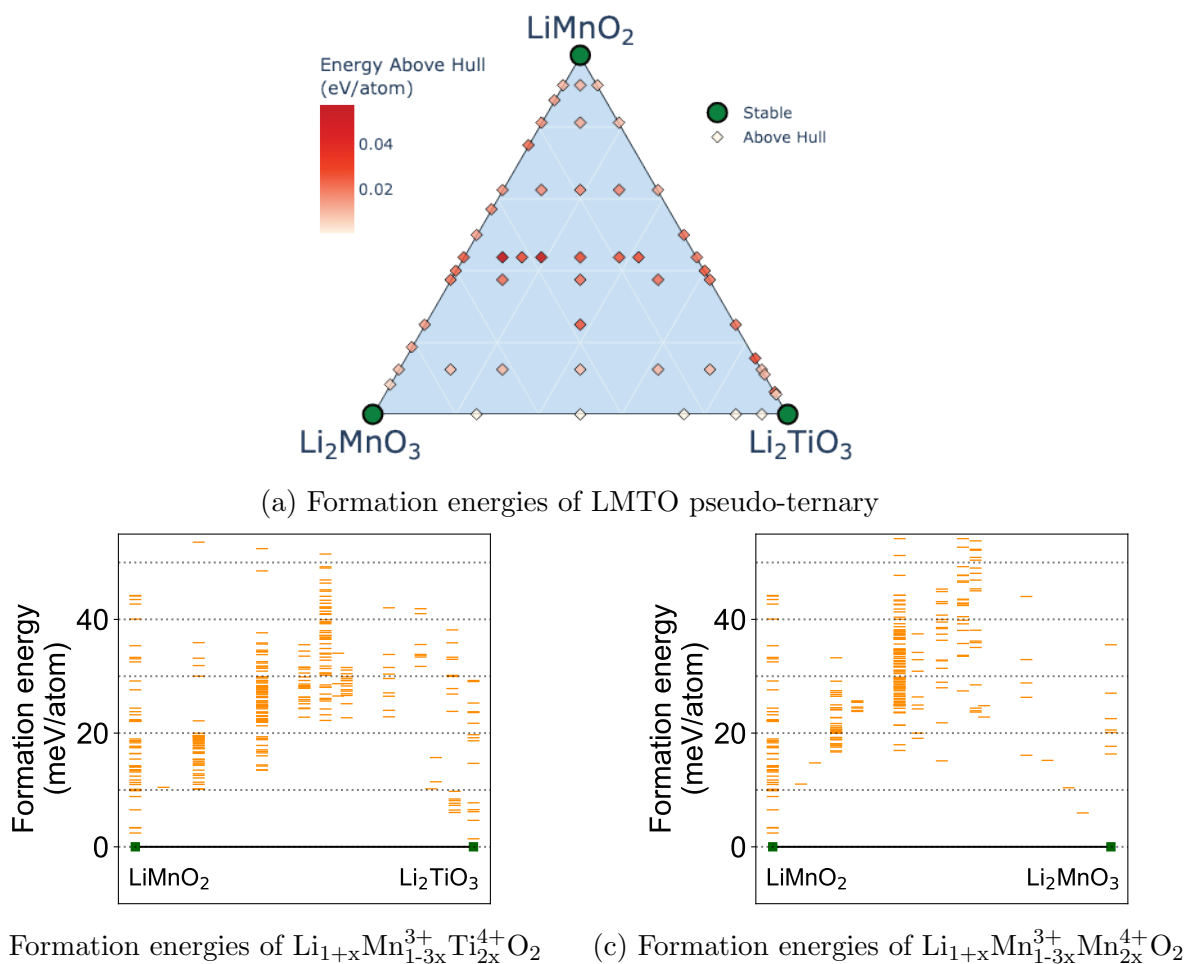


Figure 6.11: CE-computed formation energies at 0 K of the training set of LMTO rock-salt orderings. a) Formation energies of considered structures within the LMTO pseudo-ternary. b) LiMnO_2 - Li_2TiO_3 ($\text{Li}_{1+x}\text{Mn}_{1-3x}^{3+}\text{Ti}_{2x}^{4+}\text{O}_2$) and c) LiMnO_2 - Li_2MnO_3 ($\text{Li}_{1+x}\text{Mn}_{1-3x}^{3+}\text{Mn}_{2x}^{4+}\text{O}_2$) composition lines.

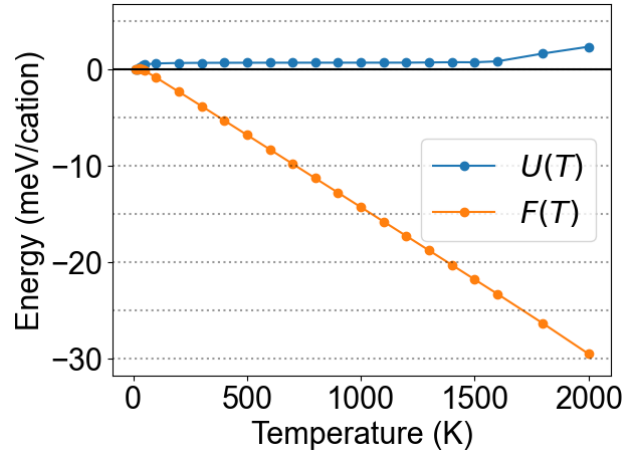


Figure 6.12: Free energy and internal energy of layered $\text{Li}_2\text{Mn}_{0.5}^{4+}\text{Ti}_{0.5}^{4+}\text{O}_3$ relative to its minimum energy, computed from canonical MC simulations.

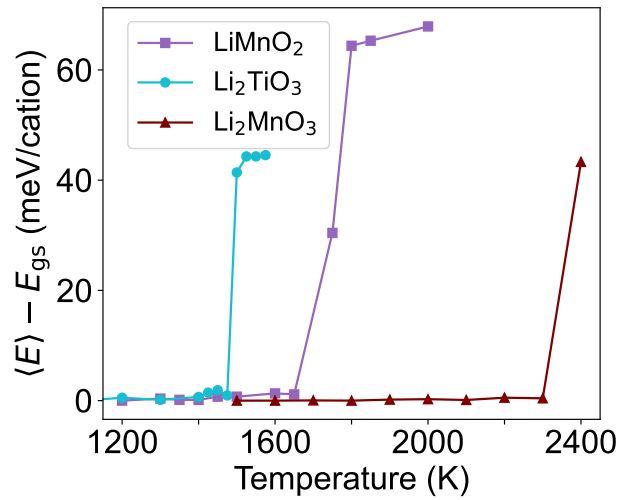


Figure 6.13: Average energies relative to the ground state energy of the ortho LiMnO_2 , layered Li_2TiO_3 , and layered Li_2MnO_3 phases, calculated using canonical MC heating simulations.

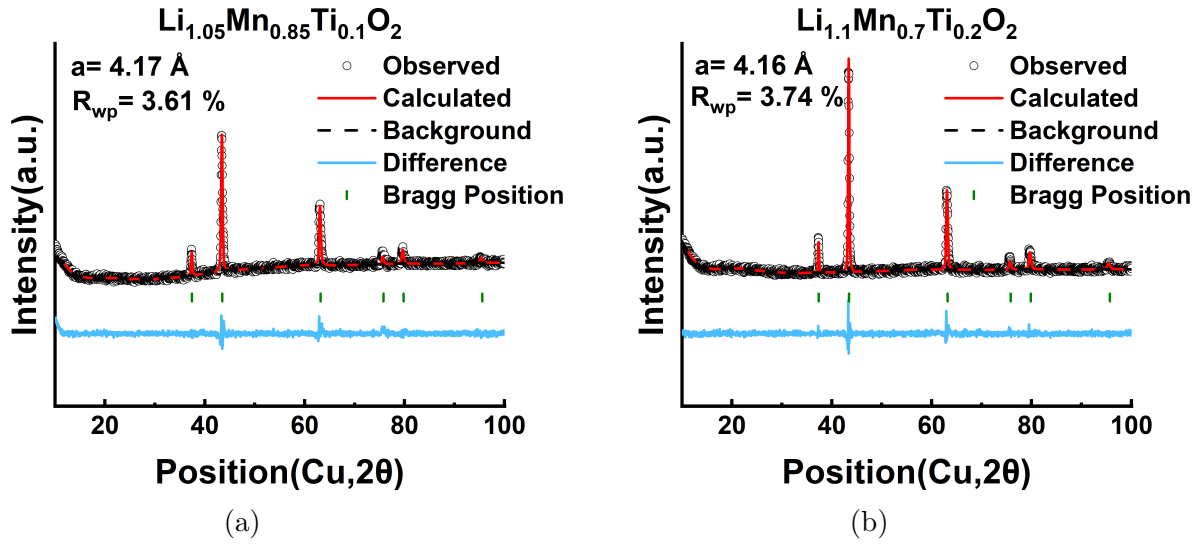


Figure 6.14: XRD patterns of compositions a) $\text{Li}_{1.05}\text{Mn}_{0.85}\text{Ti}_{0.1}\text{O}_2$, and b) $\text{Li}_{1.1}\text{Mn}_{0.7}\text{Ti}_{0.2}\text{O}_2$, quenched from 1000 °C and 900 °C, respectively. They are refined based on the rock salt structure. The lattice parameter (a) and weighted profile R factor (R_{wp}) are shown in the figures.

long-range Coulomb interactions, we parametrize an effective dielectric constant that screens the bare electrostatic interaction of idealized Li^+ , Mn^{3+} , Mn^{4+} , and Ti^{4+} point charges [35], which were calculated using the Ewald summation method [50]. The resulting CE model contains 1012 correlation functions and corresponding interactions. Mixed $\ell_1 - \ell_2$ penalized linear regression (Elastic Net [267]) is used to fit the CE on the DFT energies of 745 unique structures, where the ℓ_1 and ℓ_2 regularization terms promote sparsity and smaller magnitudes of the interactions, respectively. The training curves for ℓ_1 and ℓ_2 hyperparameter optimization are shown in Figure 6.22. The parametrized CE interactions are shown in Figure 6.20.

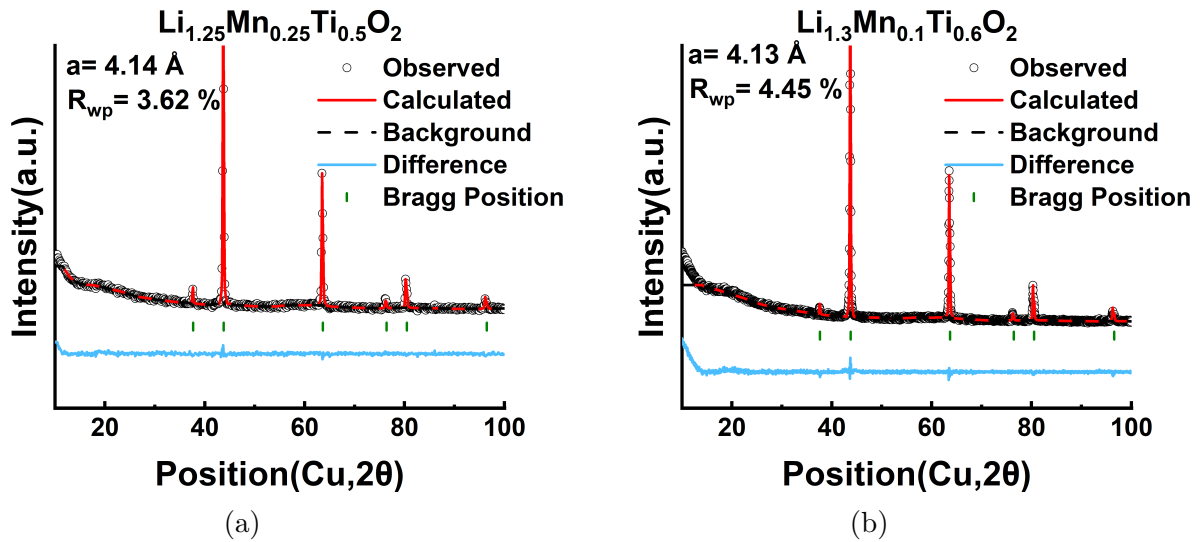


Figure 6.15: XRD patterns of compositions a) $\text{Li}_{1.25}\text{Mn}_{0.25}\text{Ti}_{0.5}\text{O}_2$, and b) $\text{Li}_{1.3}\text{Mn}_{0.1}\text{Ti}_{0.6}\text{O}_2$, quenched from 700 °C and 750 °C, respectively. They are refined based on the rock salt structure. The lattice parameter (a) and weighted profile R factor (R_{wp}) are shown in the figures.

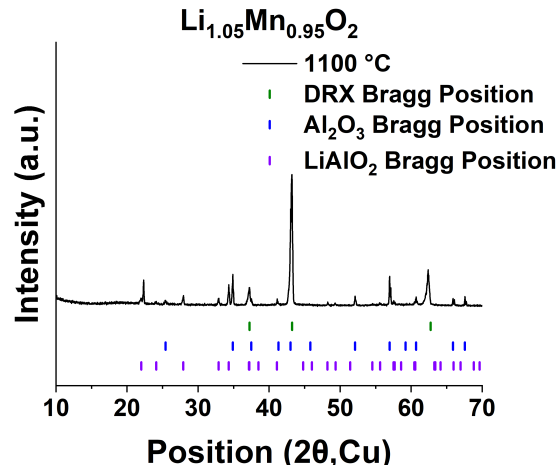


Figure 6.16: XRD pattern of the $\text{Li}_{1.05}\text{Mn}_{0.95}\text{O}_2$ sample collected at 1100 °C during the *in situ* experiment. No orthorhombic/monoclinic LiMnO_2 or layered Li_2MnO_3 phases are detected, confirming that the material is phase-pure DRX at this temperature. The additional peaks arise from the alumina sample holder and from reactions between excess Li_2CO_3 and the holder at high temperature.

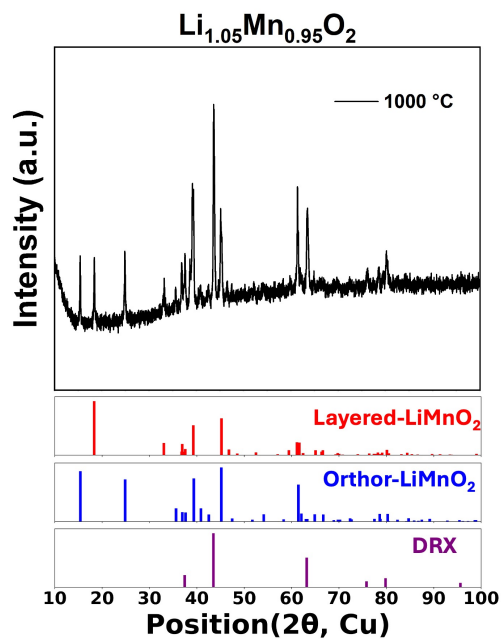


Figure 6.17: *Ex situ* XRD pattern of $\text{Li}_{1.05}\text{Mn}_{0.95}\text{O}_2$ sample quenched from 1000 °C. Layered LiMnO_2 , orthorhombic LiMnO_2 and DRX phases are observed.

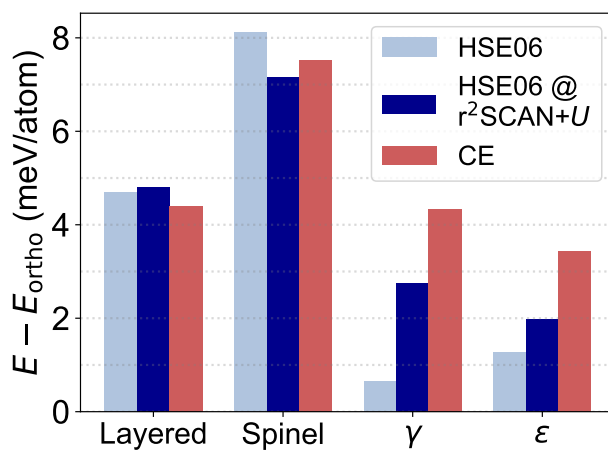


Figure 6.18: Comparison of CE and DFT energies of LiMnO_2 phases relative to ortho LiMnO_2 . These phases were previously analyzed in Chapter 5.3 and Ref. [259].

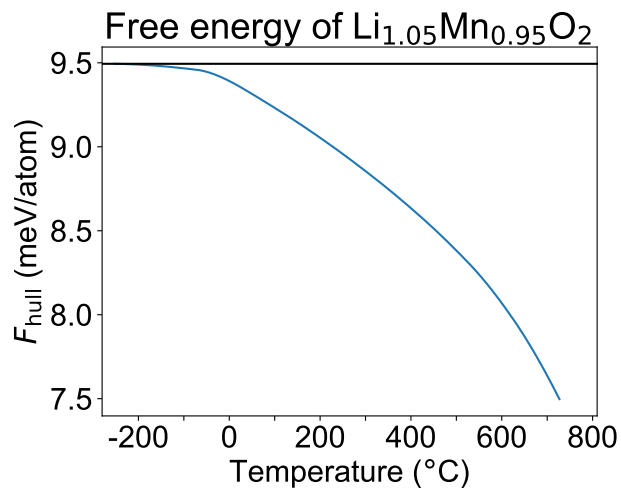


Figure 6.19: Free energy of layered $\text{Li}_{1.05}\text{Mn}_{0.85}^{3+}\text{Mn}_{0.1}^{4+}\text{O}_2$ relative to the convex hull, computed from canonical MC simulations.

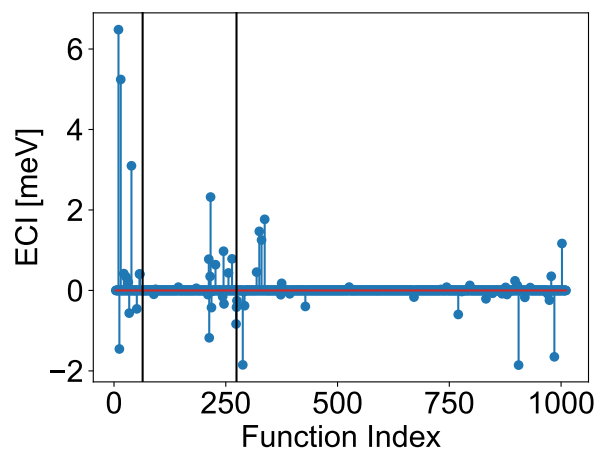


Figure 6.20: Effective cluster interactions (ECI) of the quaternary CE model. Black lines denote the division between pair, triplet, and quadruplet interactions (from left to right).

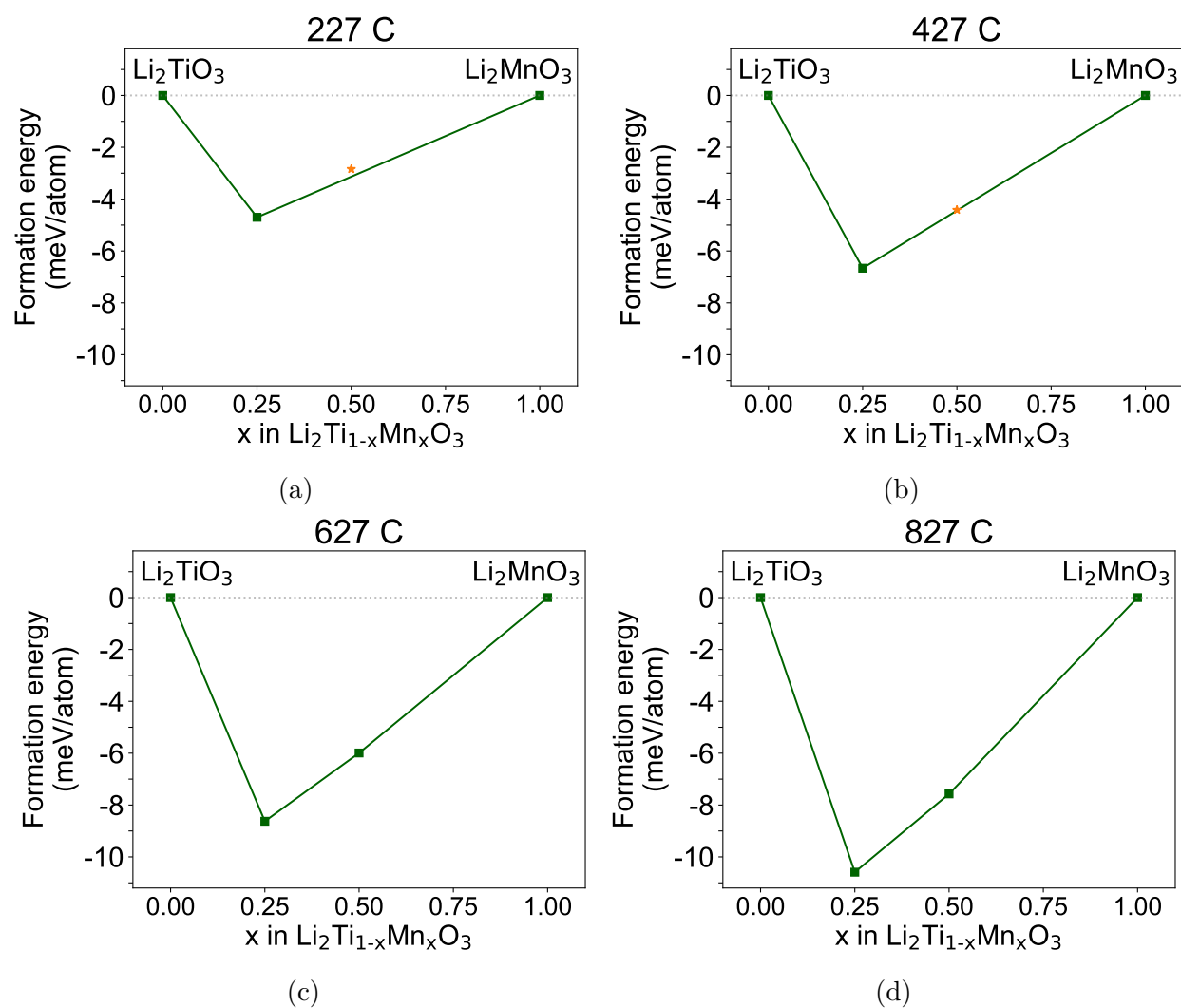


Figure 6.21: Formation energy landscape of the layered $\text{Li}_2\text{Ti}_{1-x}\text{Mn}_x\text{O}_3$ ($\text{Li}_2\text{D}^{4+}\text{O}_3$) space at varying T , computed from canonical MC simulations.

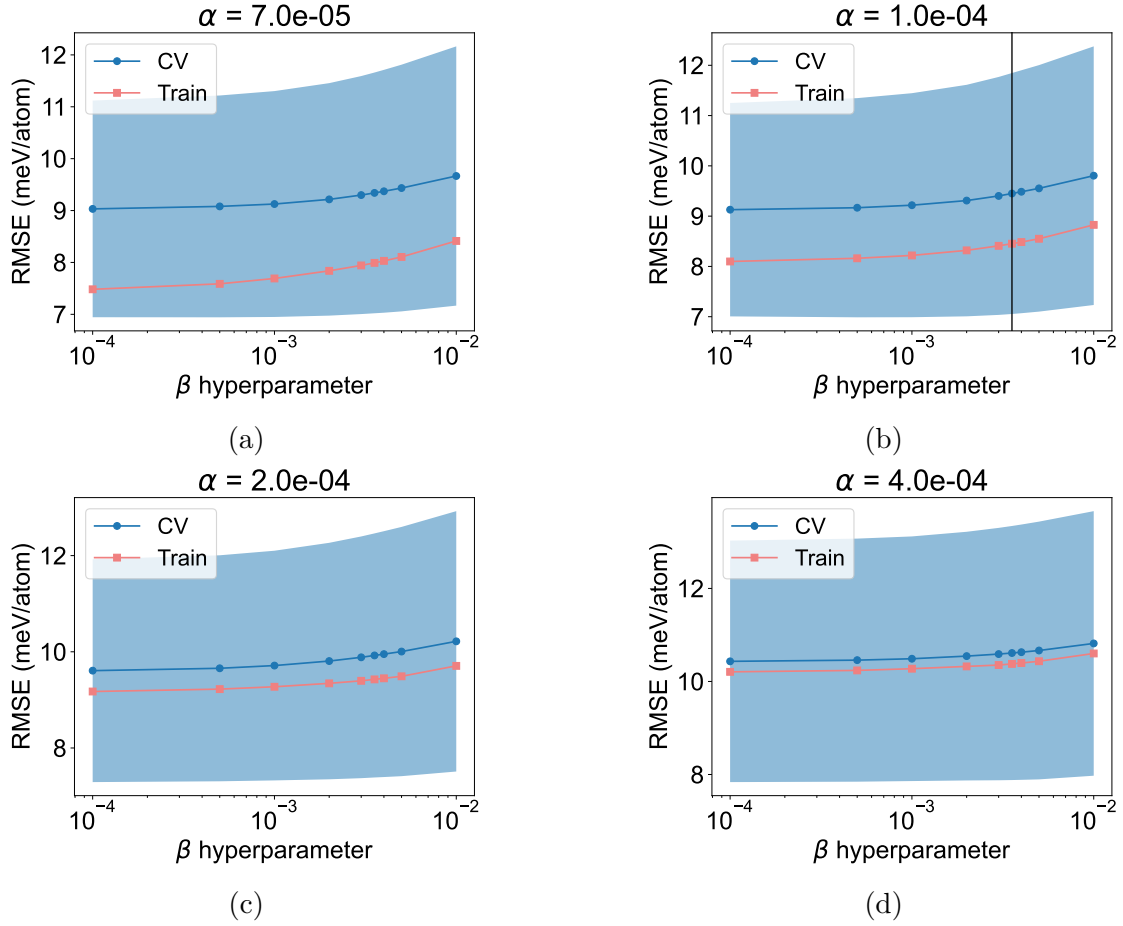


Figure 6.22: Optimizing the ℓ_1 (α) and ℓ_2 (β) regularization hyperparameters within the Elastic Net regression approach. For each α , the cross-validation (CV) and training set RMSE is plotted as a function of β . The black line denotes the chosen model, with $\alpha = 1e-4$ and $\beta = 3.55e-3$. Blue shaded regions denote the standard deviation of the 5-fold CV trials.

Chapter 7

Conclusion and Outlook

We have unraveled new understanding of the phase stability and electronic structure of LPS superionic conductors and LMTO rock-salt cathodes. Through applying a range of *ab initio* electronic structure and statistical mechanics methods, we have calculated phase diagrams of the LPS and LMTO systems, which are in reasonable agreement with the available experimental data. These phase diagrams can provide a useful guide for the future synthesis and optimization of these phases. In the LPS phase diagram, we reveal that vibrational and configuration entropy (S_{config}) are essential for describing the phase transitions among the Li_3PS_4 polymorphs. All the LPS superionic conductors are metastable at ambient temperature but exhibit significant S_{config} that helps stabilize them at high temperature, while the slow conducting phases are ordered – suggesting a correlation between the high Li S_{config} and fast Li conduction. This correlation would rationalize why compositional doping can lead to the stabilization of certain superionic conductors at lower temperature and improvements in Li mobility, a strategy which should continue to yield more promising superionic conductors for next-generation solid-state batteries.

We have derived the LMTO phase diagram using a combination of *ab initio* calculations and XRD experiments. The LMTO phase diagram is identified to be a eutectoid phase diagram, in which the T_{disord} decreases as off-stoichiometry is introduced to the end-point compositions. Importantly, this leads to a significant range of compositions with T_{disord} ranging from 680 – 900 °C, which is much lower than conventional DRX synthesis temperatures (≥ 1000 °C). Our results suggest the promise of lowering synthesis temperature for specific DRX compositions containing Ti, which can aid in the optimization of particle size/morphology, and in turn the electrochemistry of LMTO DRX. The future improvements of DRX, in conjunction with superionic conductors, can provide unprecedented Li cell energy density at low cost and the exclusive use of earth-abundant elements.

The development of physically accurate LPS and LMTO phase diagrams required extensive assessments of DFT methods to identify the approximations that reasonably capture the complex physics within these systems and importantly predict the correct ground states.

The LPS system contains relatively long-range dispersion interactions that can be reasonably captured within the r^2 SCAN meta-GGA, but not within GGA. The LMTO rock-salt phases exhibit localized $3d$ electronic states, JT distortions, and antiferromagnetism, which are not reasonably captured within GGA and meta-GGA functionals with empirical Hubbard U corrections, requiring the use of functionals with more precise self-interaction correction, such as hybrid-GGA and GGA with self-consistent Hubbard parameters. The use of inadequate DFT approximations led to the prediction of spurious ground states in both LPS and LMTO systems, highlighting the critical need to assess the accuracy of DFT methods for studying specific systems and the training of surrogate models that span these phase spaces. We have adapted the CE method to model the disorder within these materials, though with the rapid growth of machine-learned interatomic potentials (MLIPs) in recent years, it is likely that MLIPs can soon supersede CE for studying disordered materials.

It is important to point out that many recently developed MLIP models are based on GGA and meta-GGA methods, which would likely be inaccurate for classes of magnetic TM oxides similar to the LMTO system. Indeed, we have uncovered that GGA and meta-GGA with empirical Hubbard U corrections also predict a spurious ground state of the antiferromagnetic LiFeO_2 phases containing high-spin Fe, highlighting a potentially systematic shortcoming of conventional DFT(+ U) methods towards describing strongly (antiferro)magnetic materials, which can have severe implications for computational studies of materials for energy storage, quantum information, and other application areas. Given the recent growth of MLIPs in materials research, it would be essential to develop efficient schemes to parameterize these models based on more precise levels of DFT, as these methods come at greater computational cost. Furthermore, the derivation of computationally efficient electronic structure methods that can accurately describe all forms of chemical bonding on equal footing, integrated with MLIP frameworks, will be essential for developing next-generation energy materials and beyond.

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