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Revealing the Structural-Redox Interplay in the High-Voltage Spinel $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ Cathode

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Abstract

The evolution of transition metal oxide cathodes with cycling is governed by a subtle interplay between redox processes and (local) structural distortions. Here, we use first-principles calculations to monitor the electronic and structural evolution of the spinel $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ (LNMO) cathode at various stages of charge. In its $P4_332$ ordered ground state, redox-active NiO_6 octahedra are spatially isolated by redox-inactive Mn^{4+} cations, providing a clean platform to disentangle local redox and structural phenomena. By combining analyses of magnetic moments, Bader charges, and charge-density difference maps, we show that redox processes are localized on Ni, yet trigger significant transition metal-oxygen rehybridization extending to both Ni-O and Mn-O networks. Changes in oxygen charge are traced to polarization driven by evolving Ni-O bonding, rather than to anion redox activity. Concurrent structural changes include a stepwise volumetric contraction of the NiO_6 octahedra with increasing oxidation state, and Jahn-Teller distortions that are sensitively modulated by the local Li/vacancy environment. Beyond these effects, we identify additional distortion modes, including pinching deformations in both NiO_6 and MnO_6 polyhedra, which exhibit clear and systematic trends with transition metal oxidation. Together, these results

provide an atomic-level picture of coupled redox and lattice distortion processes in LNMO, revealing how Li/vacancy configurations and transition metal-oxygen rehybridization govern electrochemical behavior. The mechanisms uncovered here point to design principles that are likely to be equally critical in more complex oxide cathodes.

1 Introduction

Rechargeable lithium-ion batteries are critical to modern society, powering everything from portable electronics to electric vehicles and large-scale grid storage systems.^{1–4} The growing demand for higher energy density, longer cycle life, and lower cost continues to drive the search for advanced electrode materials. In particular, Ni-based chemistries—including layered materials such as $\text{LiNi}_x\text{Mn}_y\text{Co}_z\text{O}_2$ (NMC) and LiNiO_2 (LNO), as well as spinel $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ (LNMO)—have emerged as the leading cathode materials.^{5–8} Replacing cobalt, often found in traditional cathodes, with nickel not only reduces cost and dependence on critical raw materials but also enhances capacity, as Ni participates more extensively in the redox processes that govern charge storage.^{4,9–11}

An important topic in battery cathode research

concerns the nature of redox processes. Traditionally, charge compensation during cycling has been attributed to transition metal (TM) redox, but many high-capacity materials exhibit “excess” capacity beyond the expected TM-based capacity, which has been attributed to anion redox.^{12–16} This redox mechanism is conventionally understood as the creation of a hole on a localized oxygen orbital, usually of an oxygen ion having an “orphan” p orbital that lacks a transition metal cation to hybridize with.^{13,14} While first identified in Li-rich layered oxides,^{17–20} recent studies suggest that anion redox may also operate in stoichiometric layered compounds such as LNO, challenging the traditional view of purely cationic charge compensation.^{21,22} However, the microscopic origin of anion redox remains poorly understood,^{16,23–29} and well-defined model systems, where both redox centers and structural distortions can be unambiguously identified, are needed to disentangle the underlying mechanisms.

In addition to redox chemistry, local structural distortions play a decisive role in governing cathode performance. In TM oxides, Jahn-Teller (JT) distortions can couple electronic and lattice degrees of freedom,^{30,31} thereby affecting both electronic and ionic transport. In some materials, cooperative JT distortions drive long-range structural phase transitions,^{32,33} while in others, distortions that compromise the structural integrity of the cathode, whether reversible or irreversible, promote Li loss and accelerate capacity fade.^{34–36} Identifying how these distortions emerge and evolve during electrochemical cycling is therefore crucial for elucidating degradation pathways and guiding the design of more stable, high-performance cathode materials.

Despite its relevance as a Ni-rich layered cathode, LNO is not an ideal model system for probing the relationship between structural distortions, redox processes, and long-term cycling performance. Strong JT distortions,^{33,37,38} the presence of various defects (*e.g.* twin boundaries, antisite defects)^{39–43} and oxygen loss at high states of charge^{21,44} complicate its structural evolution and hinder efforts to directly correlate distortions with redox behavior. Moreover, LNO presents significant challenges as a computational model system for establishing this framework. Its structure

consists of edge-sharing NiO_6 octahedra arranged in layers, which makes it challenging to isolate the distortion or redox activity of a single octahedron. Furthermore, first principles calculations have shown limitations in accurately capturing its electronic structure and voltage profile.^{41–43,45,46}

Hence, we focus hereafter on the $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ (LNMO) spinel model system. LNMO is a well-studied high-voltage cathode with a robust three-dimensional framework that enables high rate performance and long cycle life.^{47–49} Notably, in the ordered spinel phase (space group $P4_332$), redox activity is restricted to isolated Ni ions ($\text{Ni}^{2+}/\text{Ni}^{3+}/\text{Ni}^{4+}$), which are exclusively surrounded by electrochemically inactive Mn^{4+} ions.^{47,50} Isolated Ni sites enable structural distortions to be directly linked to specific redox events, such as the Jahn-Teller distortion associated with Ni^{3+} ions. These decoupled sites also allow a detailed examination of electron transfer processes, helping to clarify whether redox activity is restricted to transition metal ions or involves more complex mechanisms.

In this work, we use first-principles calculations to understand redox processes and investigate their interplay with local structural distortions. We propose a redox mechanism that, while primarily centered on Ni, involves significant hybridization with O and Mn states. We identify strong correlations between Jahn-Teller distortions and the local Li-Va environment of Ni^{3+} species. We also observe that octahedral “breathing” and “pinching” mode distortions are closely related to transition metal oxidation states. Additionally, we have found a strong coupling between Li nearest neighbor hops and the surrounding Jahn-Teller distortions. These findings provide insight into how distortions and redox processes are intertwined, not only in LNMO but also in related layered cathodes such as LNO.

2 Methods

2.1 Computational details

The CASM software package^{51,52} was used to enumerate symmetrically unique vacancy orderings on the Li sublattice of the $P4_332$ LNMO spinel

crystal structure. Additionally, for every vacancy configuration, ferromagnetic and ferrimagnetic alignments of the Ni and Mn sublattices were enumerated. CASM was also used to collect and analyze collective distortion modes of NiO_6 octahedra and LiO_4 tetrahedra, as described in the Supporting Information.

Spin-polarized density functional theory (DFT) calculations were then conducted to determine the formation energies of all of the enumerated orderings of the LNMO spinel using the Vienna *ab initio* simulation package (VASP).^{53–55} Projector-augmented-wave (PAW) method pseudopotentials were used for Li, Mn, Ni, and O, with valence electronic configuration of $1s^2 2s^1$, $3p^6 3d^6 4s^1$, $3d^9 4s^1$, and $2s^2 2p^4$, respectively.⁵⁶ The r^2 -SCAN meta-generalized gradient approximation exchange-correlation functional,⁵⁷ an energy cutoff of 520 eV for the planewave basis set, a Gaussian smearing with a smearing width of 0.05 eV, and an automatic Γ -centered k -point generation scheme with a mesh spacing of $2\pi/25 \text{ \AA}^{-1}$, were employed throughout. Electronic self-consistent calculations were performed with an energy convergence threshold of 10^{-5} eV. Geometric optimizations of the crystal structures were conducted with a force convergence criterion of 0.02 eV/ $\text{\AA}$ on all ions in the unit cell. Bader charge analysis was performed using code developed by Tang et al.⁵⁸

The nudged elastic band (NEB) calculations in this work were performed using Transition State Tools for VASP.^{59–61} A conjugate gradient-based optimizer was used along with an energy convergence of 10^{-5} and a force convergence of 0.03 eV/ $\text{\AA}$ for all the NEB calculations. All other NEB DFT settings are identical to those described for other DFT calculations.

3 Results

We analyze the interplay between redox processes and local structural distortions in spinel $\text{Li}_x\text{Ni}_{0.5}\text{Mn}_{1.5}\text{O}_4$ (LNMO) as a function of Li concentration and Li/vacancy ordering. We focus in particular on $P4_332$ LNMO, the thermodynamically stable form of LNMO that emerges after a prolonged high-temperature anneal.^{50,62,63} In

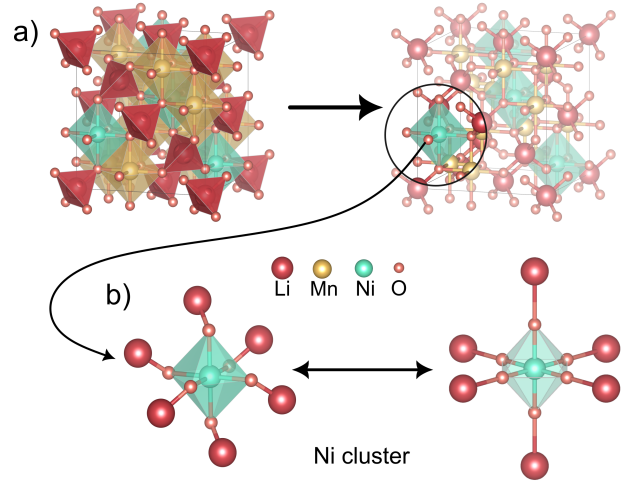


Figure 1: (a) $P4_332$ crystal structure of spinel $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$. NiO_6 octahedra (aqua) share edges with MnO_6 octahedra (light brown) and corners with LiO_4 tetrahedra (dark red). (b) The Li nearest-neighbor sites to Ni are located at an angle relative to the principal axes of the NiO_6 octahedron; for clarity, however, we depict them along the principal axes.

$P4_332$ LNMO, Ni and Mn cations form a superlattice through ordered occupation of the transition metal sites in the spinel structure. The cubic supercell of $P4_332$ LNMO (Figure 1a) contains four symmetrically equivalent Ni cations, each in an octahedral NiO_6 environment. These NiO_6 octahedra share edges with six MnO_6 octahedra, and corners with six LiO_4 tetrahedra. The NiO_6 octahedra are therefore isolated from each other. When examining the effects of different Li/vacancy orderings around a NiO_6 octahedron, each configuration is schematically represented as shown in Figure 1b (right). Most of this study focuses on the ferrimagnetic ground state, where the magnetic moments of Ni cations are antiparallel to those of Mn cations.⁶⁴

We enumerated 23 symmetrically distinct Li/vacancy orderings within the conventional unit cell of $P4_332$ LNMO (containing eight Li sites) and performed a first principles structural relaxation for each configuration. From the relaxed structures, we extracted the local collinear magnetic moments, quantified distortions of the NiO_6 and MnO_6 octahedra as well as the LiO_4 tetrahedra, and computed Bader charges for all ions.

3.1 Redox mechanisms in $P4_332$ LNMO

First, we examine Li, Ni, Mn and O magnetic moments and Bader charges, and construct charge-difference maps to elucidate redox processes in spinel $\text{Li}_x\text{Ni}_{0.5}\text{Mn}_{1.5}\text{O}_4$. Our analysis focuses on the lowest energy Li/vacancy configuration at each composition considered (i.e. $x=0$ to 1 in steps of $1/8$).

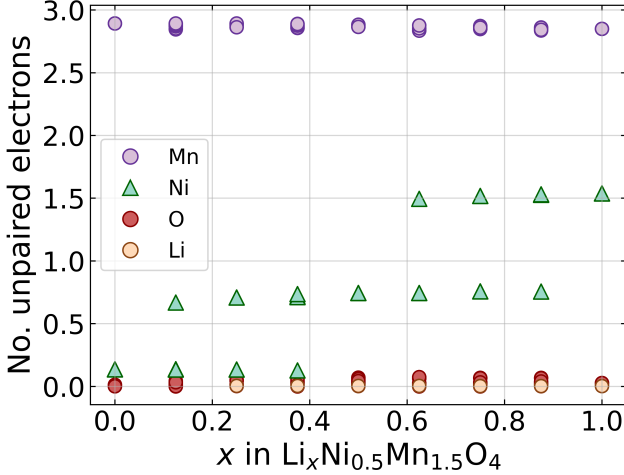


Figure 2: Number of unpaired electrons on each ion in spinel $\text{Li}_x\text{Ni}_{0.5}\text{Mn}_{1.5}\text{O}_4$ calculated using $r^2\text{SCAN}$ for the lowest energy Li/vacancy configuration at each composition considered (i.e. $x=0$ to 1 in steps of $1/8$).

Figure 2 shows the number of unpaired electrons on each ion in LNMO, calculated with $r^2\text{SCAN}$. For a given species (e.g. Ni), multiple data points at a particular Li content arise from different local environments within the lowest-energy Li/vacancy configuration. The number of unpaired electrons on Li, Mn and O remains largely unchanged with Li concentration, consistent with the formal oxidation states Mn^{4+} , Li^+ , and O^{2-} . For Mn^{4+} in a high spin configuration, three unpaired electrons occupy the t_{2g} orbitals, leaving the t_{2g} manifold half-filled. Unlike Li, Mn and O, the unpaired electron count on Ni changes with Li concentration, suggesting that redox processes are confined to the Ni cations. At low Li concentrations ($x \leq 3/8$), some Ni cations exhibit nearly zero unpaired d electrons, consistent with a low-spin Ni^{4+} state in which the t_{2g} orbitals are fully occupied and the e_g orbitals are empty.

At intermediate compositions ($1/8 \leq x \leq 7/8$), some Ni ions have approximately 0.7 unpaired electrons, in agreement with a formal Ni^{3+} state where one unpaired electron resides in an e_g orbital. Above $x \geq 5/8$, some Ni ions exhibit approximately 1.5 unpaired electrons, a value close to two and consistent with a formal Ni^{2+} state in which two electrons occupy the e_g orbitals.

An alternative approach to probing redox behavior is Bader charge analysis, which integrates the DFT electron density within atomic basins defined by zero-flux surfaces in the charge density.⁵⁸ To understand the oxidation states found in this material, we define the *excess* Bader charge as the difference between the Bader charge of an ion and that of the corresponding neutral atom.

The calculated excess Bader charges for Mn, Ni and O are shown in Figures 3a, 3b and 3c. Li is not included because its excess charge shows negligible variation with composition and remains close to 0.9. As expected, anions carry negative excess Bader charges, while cations carry positive values. The excess Bader charge on Mn (≈ 1.9) is substantially smaller than the formal 4+ oxidation state inferred from the number of unpaired electrons in Figure 2. Although a slight dependence on Li concentration can be observed in Figure 3a, the magnitude of this change is minimal compared to the variations observed for Ni and O.

In contrast to Mn, excess Bader charges for Ni species cluster into three distinct bands, mirroring the trend observed for the number of unpaired electrons (Figure 2). These Ni excess charges—approximately 1.47, 1.38 and 1.2—are again significantly smaller than the corresponding formal oxidation states of Ni^{4+} , Ni^{3+} and Ni^{2+} , respectively. The small variation of the Bader charge over different formal oxidation states can be attributed to a “negative-feedback charge regulation” phenomenon.⁶⁵

Similar to Ni, the excess Bader charge on O varies substantially with Li concentration (Figure 3c). However, the numerical values remain smaller than the formal 2- oxidation state typically assigned to oxide ions. Figure 3c further shows that the O excess Bader charge depends strongly on the local environment. Each O ion in the spinel structure is tetrahedrally coordinated

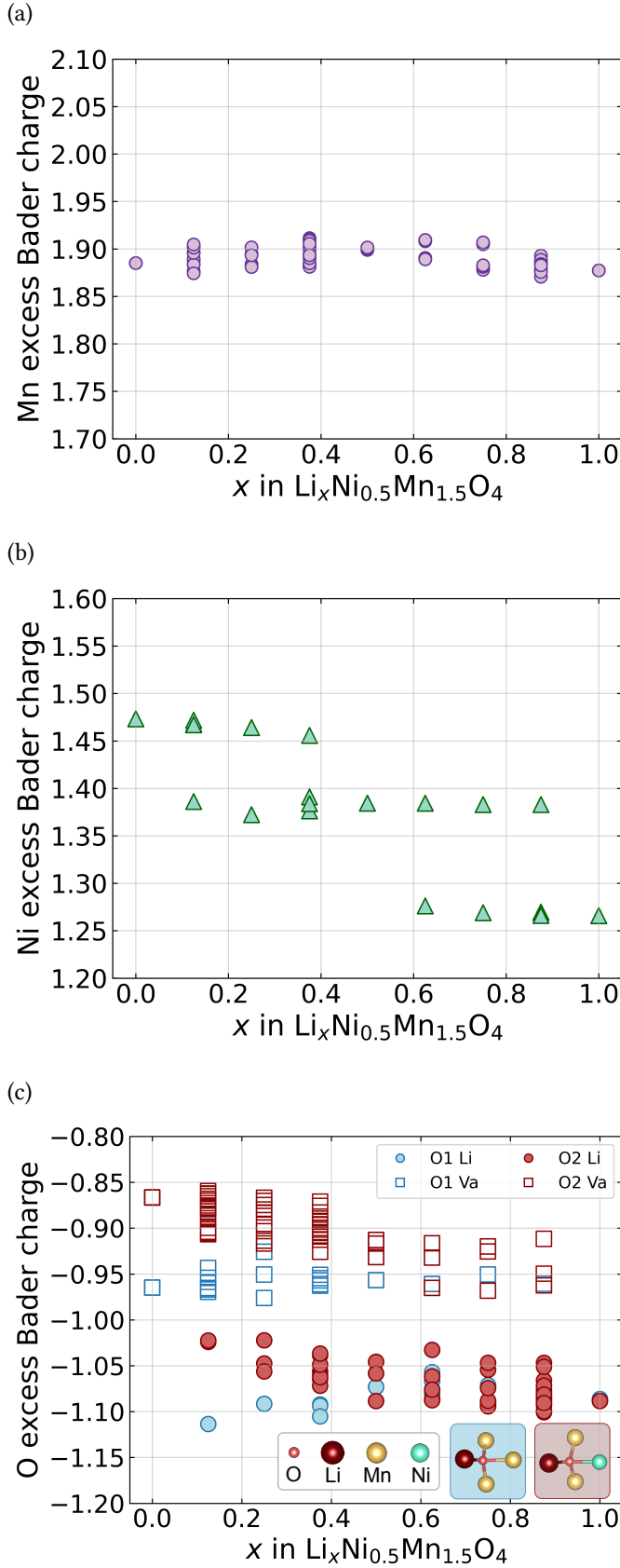


Figure 3: Excess Bader charge (difference between the Bader charge of an ion and that of the corresponding neutral atom) for (a) Mn, (b) Ni, and (c) O ions in the lowest-energy Li/vacancy (Va) configuration at each Li composition. In (c) O ions are labeled by symmetrically unique sites (coordinated to Mn only (blue) or Mn and Ni (red)) and by Li/Va (circle/square) coordination.

to three transition metals and one Li. In $P4_332$ LNMO, two symmetrically distinct O sites exist: one coordinated to both Mn and Ni, and another coordinated exclusively to Mn (insets in Figure 3c). O sites can further be distinguished by whether the adjacent Li site is occupied. Figure 3c shows that O ions adjacent to Li exhibit more negative excess Bader charges than those adjacent to a Li vacancy. Upon delithiation, O ions coordinated only to Mn carry a more negative excess Bader charge than those with a Ni neighbor.

Although the large changes in the O excess Bader charge with Li concentration suggest that O anions participate in the redox process along with the Ni cations, an analysis of charge difference plots suggests a more subtle and nuanced redox mechanism that involves a substantial degree of rehybridization between transition metal and oxygen ions. In an octahedron with cubic symmetry, the TM d_{z^2} and $d_{x^2-y^2}$ orbitals hybridize with coordinating oxygen p orbitals to form a pair of σe_g^b bonding orbitals and a pair of σe_g^* anti-bonding orbitals (red orbitals in Figure 4). The t_{2g} TM d_{xy} , d_{yz} and d_{xz} orbitals also hybridize with coordinating oxygen p orbitals (blue orbitals in Figure 4) to form weaker π bonds. The bonding e_g^b orbitals tend to have more of an oxygen p character with a larger fraction of charge residing on oxygen than on the TM. The anti-bonding e_g^* orbitals, in contrast, have more of a TM d character. The degree to which the charge densities of the bonding and anti-bonding states are polarized depends on how covalent versus ionic the bonds are. In high oxidation states (such as Ni^{4+}) the e_g^b states are more covalent, with charge shared more uniformly between the TM and O. When an electron is added to an anti-bonding e_g^* orbital during redox, the e_g^b bond polarizes and becomes more ionic, with charge of the bond shifting away from the TM and towards the oxygen. This is because the addition of an electron to the e_g^* orbital increases electrostatic interactions between electrons on the TM, which can be reduced by rehybridizing the e_g^b orbital through the displacement of the charge density that was originally on the TM towards the oxygen. The net effect of adding an electron to the e_g^* orbital is that less than one electron of charge will emerge on the TM and the electron density on O will increase. This redox

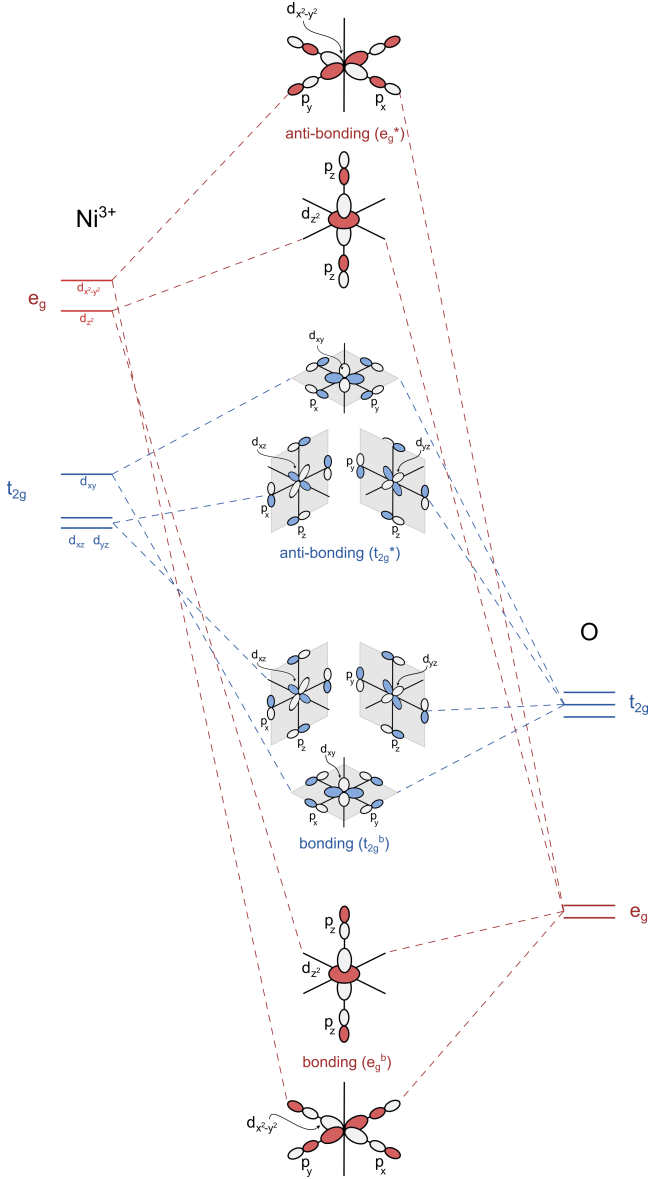


Figure 4: Hybridization diagram for a Jahn-Teller z -elongated octahedron containing Ni^{3+} d orbitals and O p orbitals. Bonding (anti-bonding) hybridized orbitals are denoted by matching (non-matching) phases in the either head-on-head (σ) or side-by-side (π) orbital overlap. Note that this is a simplified hybridization diagram to illustrate bonding and anti-bonding e_g and t_{2g} orbitals, and orbitals with a_{1g} and t_{1u} symmetry are not depicted. For a non-Jahn-Teller-distorted octahedron, (e.g. $\text{Mn}^{\text{IV}}\text{O}_6$), this hybridization diagram would look largely the same, with the exception that the e_g and t_{2g} orbitals on the TM would be energetically degenerate, respectively.

induced rehybridization is evident in the charge difference plots of Figure 5 and Figure S1.

As an illustrative case, we examine in detail the charge density difference between the $\text{Li}_{1/8}\text{Ni}_{0.5}\text{Mn}_{1.5}\text{O}_4$ and $\text{Ni}_{0.5}\text{Mn}_{1.5}\text{O}_4$ compositions within a plane containing a central Ni ion, two of its nearest-neighbor Mn ions, along with the bridging O ions (Figure 5(a)). In this comparison, the Ni, Mn and O atomic positions are kept fixed and correspond to those of $\text{Li}_{1/8}\text{Ni}_{0.5}\text{Mn}_{1.5}\text{O}_4$ in which all the oxygen ions form a perfect cubic FCC sublattice, with the exception of the oxygen ions surrounding the one Ni having a Ni^{3+} formal oxidation state. The oxygen coordinating this Ni^{3+} are displaced to produce a positive Jahn-Teller distortion, with the long axis pointing out of the page. The charge difference plot shows where the electron donated by the intercalated Li localizes and how its addition drives charge redistribution throughout the crystal. In the isosurface plot of Figure 5(a)i, charge accumulation and depletion are shown in yellow and light blue, respectively, while the slices shown in Figure 5(a)ii use red and navy blue to denote the same features.

The charge difference map in Figure 5(a) shows significant redistribution of charge density across the Ni, Mn and O valence orbitals upon the addition of a Li. Figure 5(a)i shows an accumulation of charge density on Ni in the yellow region resembling a d_{z^2} orbital pointing out of the page. This charge distribution has the shape of the anti-bonding e_g^* orbital that is stabilized by a positive Jahn-Teller distortion in the $\hat{z}$ direction and emerges upon hybridizing the orbitals shown in Figure 4. The addition of an electron to this e_g^* orbital effectively generates a reduced Ni^{3+} species. Figures 5(a)i and (a)ii also show a depletion of charge in the clover-leaf-shaped blue region resembling a $d_{x^2-y^2}$ orbital surrounding Ni. In parallel, there is an accumulation of charge on p orbitals pointing to Ni and residing on the four coordinating oxygen ions. This signifies a rehybridization of the e_g^b orbital formed from the orbitals of Figure 4. Due to the addition of an electron to the d_{z^2} -shaped e_g^* anti-bonding orbital, charge is displaced from the $d_{x^2-y^2}$ orbitals to the O p orbitals, resulting in a more ionic polarization of the e_g^b bond to reduce electrostatic interactions between electrons on Ni.

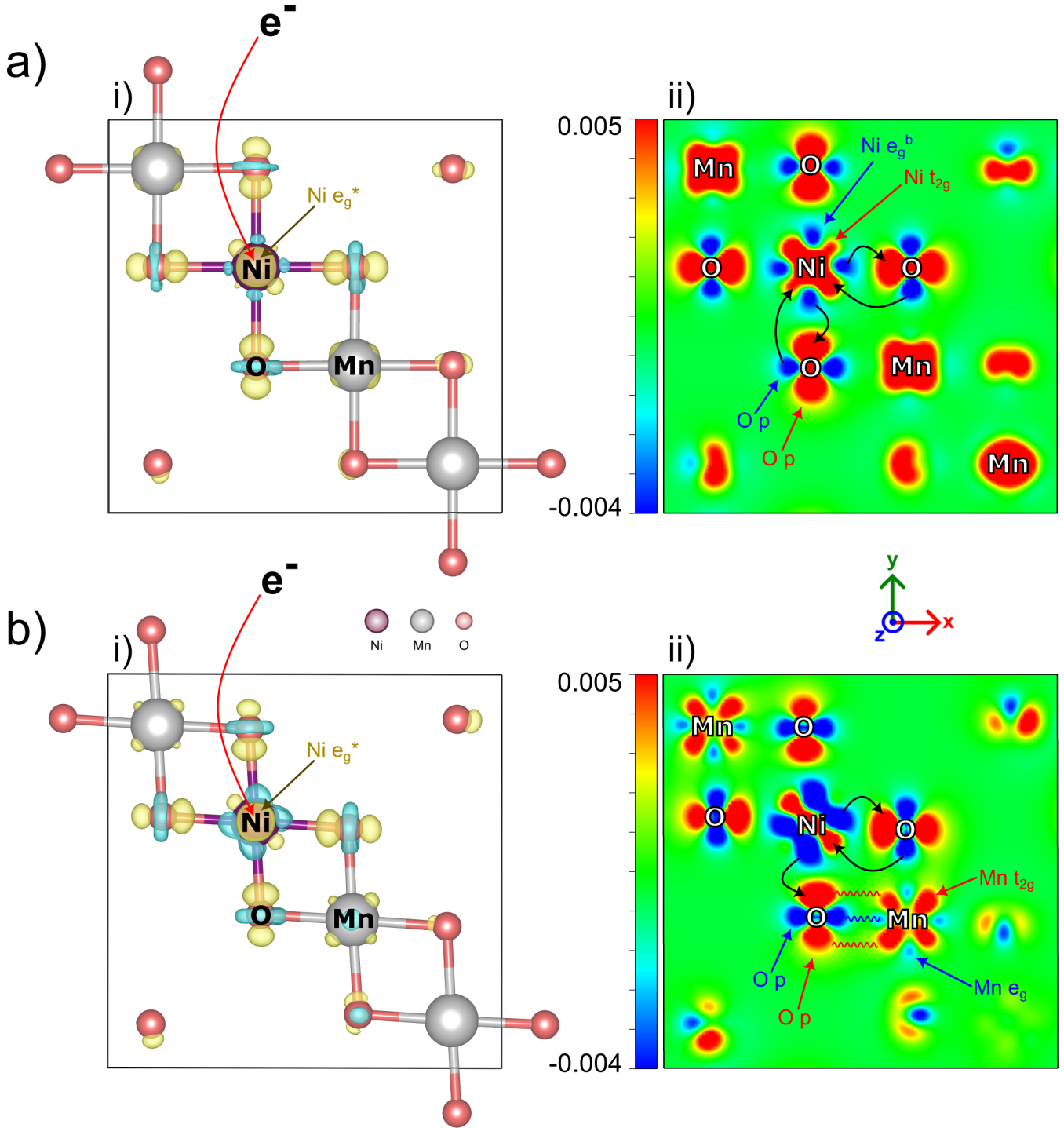


Figure 5: Two-dimensional charge difference maps around a Jahn-Teller active Ni^{3+} ion obtained between the $\text{Li}_{1/8}\text{Ni}_{0.5}\text{Mn}_{1.5}\text{O}_4$ and $\text{Ni}_{0.5}\text{Mn}_{1.5}\text{O}_4$ compositions. In (a), the $\text{Li}_{1/8}\text{Ni}_{0.5}\text{Mn}_{1.5}\text{O}_4$ reference structure is a cubic spinel with only the central Ni ion in the plane residing in a Jahn-Teller distorted octahedron. In (b), the $\text{Li}_{1/8}\text{Ni}_{0.5}\text{Mn}_{1.5}\text{O}_4$ reference structure has been fully relaxed and contains Jahn-Teller and pinching distortions. The long axis of the Jahn-Teller distortion points out of the plane in both (a) and (b). The charge difference maps are either represented (i) as a slice or (ii) as an isosurface. Seen in this figure are in-plane Ni e_g^b and t_{2g} orbitals. There is also an $e_g^* d_z^2$ along the Jahn-Teller long axis coming out of the plane, which is seen only in part (i) for both (a) and (b). An electron is added to this e_g^* orbital when Li is inserted and thus induces the rehybridization process. In parts (i) yellow (light blue) and (ii) red (navy blue) regions indicate charge accumulation (charge depletion) regions.

In addition to a rehybridization of the e_g^b orbitals, Figures 5(a)i and (a)ii also show a slight charge accumulation around Ni in a pattern that resembles a d_{xy} orbital. In parallel, there is a depletion of charge on oxygen p orbitals that form π bonds with a Ni d_{xy} orbital. This charge redistribution suggests a rehybridization of the π bonds formed by the orbitals of Figure 4, with charge displaced from oxygen p orbitals to the d_{xy} orbital on Ni. The driving force for this charge redistribution presumably has an electrostatic origin, with the accumulation of charge on the oxygen p orbitals pointing to Ni, due to rehybridization of e_g^b , displacing charge on the orthogonal oxygen p orbitals. Note that the accumulated charge distribution on Ni in a d_{xy} -like orbital is slightly skewed, with more charge density along the axis connecting neighboring Mn cations than on the perpendicular axis. The cation arrangement in spinel breaks the local cubic symmetry of the TM octahedra, which in turn lowers the symmetry of the electronic orbitals. Finally, Figures 5(a)i and (a)ii show an accumulation of charge on Mn with a distribution that resembles a d_{xy} orbital. There is also very faint depletion on Mn in the shape of a t_{2g} orbital.

Figure 5(b)i and ii show similar charge difference plots calculated using the coordinates of fully relaxed $\text{Li}_{1/8}\text{Ni}_{0.5}\text{Mn}_{1.5}\text{O}_4$. The symmetry of the spinel crystal structure allows for relaxations that break the perfect cubic symmetry of the TMO_6 octahedra (or the tetragonal symmetry of the Jahn-Teller distorted octahedron). This is evident in Figure 5(b)i, where the angles between adjacent pairs of Mn-O or Ni-O bonds are no longer 90° . The lower symmetry of the distorted NiO_6 and MnO_6 octahedra increases the degree of rehybridization and modifies the shapes of the orbitals that gain and lose charge upon the addition of Li. While there is still a substantial accumulation of charge on the out-of-plane d_{z^2} -like lobe, the Ni in-plane lobes directed toward the Mn exhibit increasingly pronounced charge accumulation.

Interestingly, the charge difference maps of the fully relaxed structure indicate that charge accumulation on oxygen—arising from rehybridization of the Ni-O bonds—extends to adjacent Mn-O bonds. This secondary effect redistributes charge

among the Mn valence orbitals, even though the Mn excess Bader charge and magnetic moment change very little with Li insertion. Specifically, electron density accumulates in the in-plane Mn t_{2g} orbitals, whereas the in-plane e_g^b orbitals, formed through the hybridization between O p and Mn $d_{x^2-y^2}$ orbitals (Figure 4(b)) and pointing toward the bridging O ions, are depleted. This result can be rationalized by considering charge accumulation on the O p orbitals oriented toward Ni. The added electron density increases Coulomb repulsion with electrons in the orthogonal in-plane O p orbitals, (which point towards Mn), as discussed above. Because these orthogonal O p orbitals participate in σ -type bonding with the Mn $d_{x^2-y^2}$ orbitals, the enhanced repulsion drives rehybridization of the Mn-O bond. This process leads to depletion of electron density in both the Mn $d_{x^2-y^2}$ and the interacting O p orbitals, as indicated by the wavy blue line in Figure 5(a)ii. Consequently, electron density on Mn shifts from the $d_{x^2-y^2}$ to the d_{xy} orbital, as is evident from the red clover-leaf feature in the diagram. The increased occupancy of the d_{xy} orbitals, which is part of the t_{2g} manifold, enhances π -type interactions with neighboring O ions (Figure 4(c)), as illustrated by the wavy red lines in Figure 5(a)ii.

Charge difference plots at other Li concentrations are shown in Figure S1 and reveal similar rehybridization behavior.

3.2 Polyhedral Distortions and Their Local Environments

The results presented in the previous section consistently show that redox processes in $\text{Li}_x\text{Ni}_{0.5}\text{Mn}_{1.5}\text{O}_4$ involve some transfer of electron density to and from the Ni e_g^* states, although the specific details depend on the analytical method used. This electron transfer, in turn, triggers the rehybridization of Ni-O and Mn-O bonds within the local octahedral network. Redox reactions and associated changes in bonding can lead to measurable structural changes, including symmetry breaking distortions. In this section, we examine how redox processes affect the amplitudes of symmetry-adapted displacement modes of NiO_6 octahedra, and how these distortions cor-

relate with the surrounding Li/vacancy ordering. To achieve this, the amplitudes of the symmetry-adapted collective distortion modes were calculated following the approach of Saber et al.⁶⁶ and as detailed in Section 1 of the Supporting Information.⁶⁷ Figure S2 illustrates how all distortion modes in a crystal were mapped onto a prototype cluster.

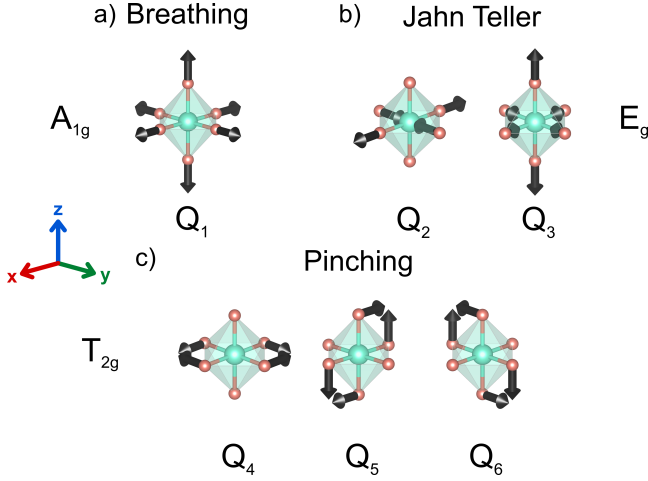


Figure 6: Normal mode distortions studied in this work: (a) breathing mode with A_{1g} symmetry composed of the Q_1 normal mode with amplitude q_1 , (b) Jahn-Teller modes with E_g symmetry, composed of the Q_2 and Q_3 normal modes with amplitudes q_2 and q_3 respectively, and (c) pinching modes with T_{2g} symmetry, composed of Q_4 , Q_5 , and Q_6 normal modes with amplitudes q_4 , q_5 , and q_6 respectively.

Across all Li compositions examined in this work, we find that three types of distortion modes (relative to the ideal cubic octahedron reference state) exhibit non-negligible amplitudes: a volumetric mode, also known as "breathing" mode (Figure 6a), two-dimensional E_g Jahn-Teller modes, (Figure 6b), and three-dimensional pinching modes (Figure 6c).^{51,66} The volumetric mode with amplitude q_1 describes a symmetry-preserving volumetric expansion or contraction of the octahedron. The Jahn-Teller modes, with amplitudes q_2 and q_3 , together describe tetragonal and orthorhombic distortions of the cubic reference octahedron. A positive q_3 amplitude produces an elongation of the octahedron along the z -direction and a simultaneous contraction along the x and y axes, as illustrated in Figure 6b.

This is commonly referred to as a positive E_g Jahn-Teller distortion. A negative q_3 reverses the direction of these distortions to generate a negative Jahn-Teller distortion. The q_2 amplitude produces distortions within the x and y planes, with an elongation (contraction) along the x axis coupled with an equal contraction (elongation) along the y axis. Together, q_2 and q_3 generate all symmetrically-equivalent E_g Jahn-Teller distortions of the cubic octahedron, as illustrated in (Figure S3). Finally, the pinching modes with amplitudes q_4 , q_5 , and q_6 distort the octahedron by bringing two axes closer together while leaving the third axis largely unchanged, as illustrated in Figure 6c. An equal combination of all three amplitudes (q_4 , q_5 , and q_6) generates a rhombohedral distortion of an octahedron.

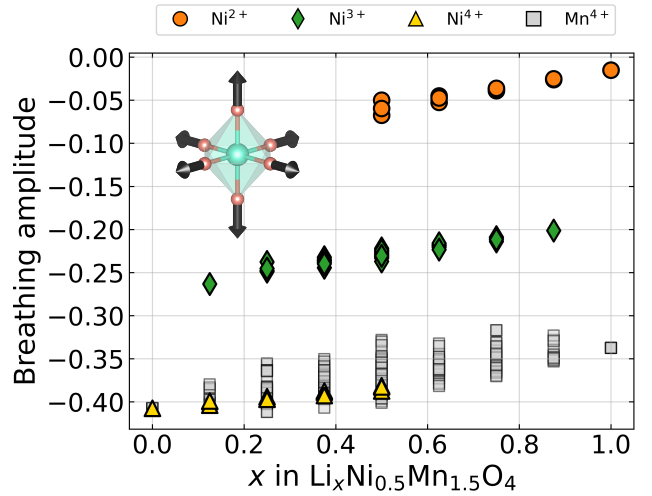


Figure 7: Breathing mode amplitudes of Ni and Mn octahedra in ferrimagnetic LNMO.

Figure 7 shows the amplitudes of the breathing modes of Ni and Mn polyhedra in the ferrimagnetic $P4_332$ structure as a function of Li composition. Each data point corresponds to an individual Ni (or Mn) polyhedron, and is labeled according to its oxidation state, as determined from the number of unpaired electrons (see previous section). As evidenced by the distinct groupings by oxidation state, the Ni octahedra expand in discrete steps as Li insertion drives Ni reduction. By contrast, Mn remains Mn^{4+} throughout, and any expansion of the Mn octahedra is minimal relative to the pronounced Ni response.

Octahedrally-coordinated transition metals with one electron in their e_g^* levels, such as Ni^{3+} ,

are Jahn-Teller distorted, while species with an even number of electrons in those levels, such as Ni^{2+} and Ni^{4+} , are not.^{31,68} Figure 8 shows the q_2 and q_3 amplitudes of each NiO_6 octahedron for all fully relaxed $\text{Li}_x\text{Ni}_{0.5}\text{Mn}_{1.5}\text{O}_4$ supercells considered in this study. The amplitudes of the symmetrically equivalent positive (negative) Jahn-Teller distortions, which can occur along the cubic x , y or z axes, are represented in q_2 - q_3 space by the red (blue) lines in Figure 8. As expected, the q_2 and q_3 amplitudes of Ni^{3+} octahedra (green) are significantly larger than those of Ni^{2+} and Ni^{4+} octahedra (orange and yellow in Figure 8), and we focus our attention on the distortions around Ni^{3+} species hereafter. The majority of the Ni^{3+} octahedra undergo a positive Jahn-Teller distortion with their q_2 and q_3 amplitudes clustering close to the red lines. In contrast, there are very few examples of negative Jahn-Teller distortions with amplitudes close to the blue lines. Interestingly, several Ni^{3+} species show a mixture of positive and negative Jahn-Teller distortions, with amplitudes q_2 and q_3 residing between the red and blue lines.

A convex hull diagram of the Li/vacancy configurations at Li contents $x=0$ to 1 (in increments of 1/8) is shown in Figure S4. The distortions of the four Ni octahedra in the unit cell are color-coded according to the Jahn-Teller distortion type for each Li/vacancy configuration in Figure S4. Figure S5 shows the Jahn-Teller distortion amplitudes for both ferrimagnetic configurations (Ni and Mn cations with antiparallel moments) and ferromagnetic configurations (all transition metal moments aligned) of the $P4_332$ structure. The Jahn-Teller distortions are consistently larger in the ferromagnetic cell than in ferrimagnetic one.

In Figure 8, diamonds, triangles and squares are used to distinguish amplitudes of NiO_6 octahedra surrounded by two, three and four lithium vacancies, respectively. The distortions of octahedra surrounded by three vacancies (triangles) are always close to a red line, i.e., a pure positive Jahn-Teller distortion. NiO_6 octahedra surrounded by two vacancies generally show a positive Jahn-Teller distortion, although some exhibit a negative distortion. Finally, octahedra surrounded by four vacancies often exhibit mixed Jahn-Teller distortions with amplitudes residing between the red

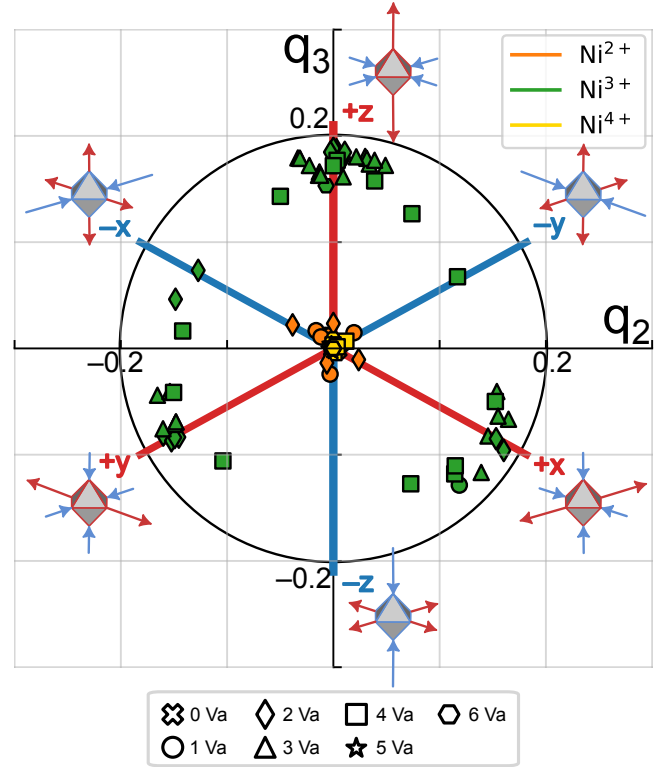


Figure 8: Jahn-Teller distortion amplitudes of Ni octahedra in ferrimagnetic LNMO, plotted as a function of their assigned oxidation state.

and blue lines.

The Jahn-Teller distortion adopted by a given NiO_6 octahedron depends sensitively on its local Li/vacancy configuration (Figure 9):

- (1) Collinear Li vacancies: When two Li vacancies occupy diametrically opposed sites (at 180°) along a single axis of a NiO_6 octahedron, they induce contraction along that axis.
- (2) Collinear Li ions: Conversely, when the two diametrically opposed Li sites are filled, the NiO_6 octahedron elongates along the axis connecting them. If more than one axis contains collinear Li ions, at least one such axis will undergo elongation.
- (3) Frustration: In many cases, the NiO_6 octahedron exhibits mixed occupation of opposite Li sites along different axes, leading to structural frustration. When multiple equivalent axes are present, one axis typically elongates while the other(s) contract. The octahedron preferentially distorts in a

manner that maximizes the number of axes compressed along vacancy directions.

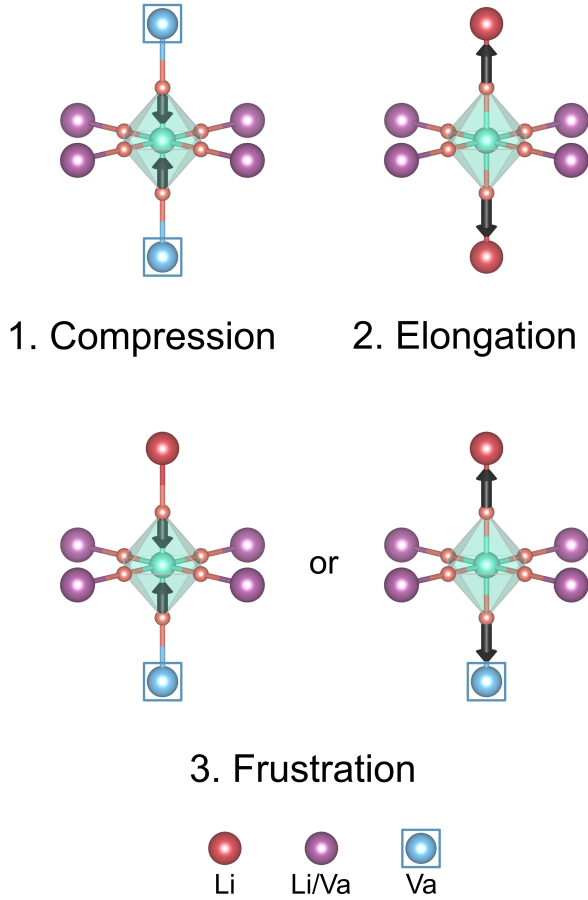


Figure 9: Trends in the distortion behavior of NiO_6 octahedra as a function of the Li/vacancy environment: 1) Diametrically opposed Li vacancies result in compression along that axis. 2) Diametrically opposed occupied Li sites lead to elongation along that axis. If more than one such axis is present, at least one axis will elongate. 3) When mixed occupation of opposite Li sites occurs along different axes, the NiO_6 octahedron distorts to maximize the number of axes compressed along Li vacancy directions.

These trends outlined above and schematically illustrated in Figure 9 are derived from an analysis of 54 Ni^{3+} octahedra across 23 optimized $\text{Li}_x\text{Ni}_{0.5}\text{Mn}_{1.5}\text{O}_4$ structural models, which encompass various Li/vacancy orderings and Li concentrations. Figure 10 summarizes the range of observed Li/vacancy configurations around NiO_6 octahedra and the corresponding octahedral distortion mode.

Unique JT Distortion Configuration			
0 Va			6 Va
1 Va			5 Va
2 Va	a	 	4 Va
	b		
3 Va	c	d	3 Va

Figure 10: Unique Li/vacancy NiO_6 octahedra and their associated Jahn-Teller distortions, grouped by the number of vacant Li sites.

No significant octahedral distortion is expected for the limiting configurations with either no Li vacancy (0 Va) or no Li (6 Va) present around the central Ni (top row in Figure 10), since Ni adopts the 2+ or 4+ oxidation state in these cases. This expectation is borne out in $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$, which contains no vacancy environments. We find, however, that a 6 Va environment in $\text{Li}_{1/8}\text{Ni}_{0.5}\text{Mn}_{1.5}\text{O}_4$ exhibits a positive Jahn-Teller distortion, indicating that at dilute Li concentrations, NiO_6 octahedra containing Ni^{3+} are not necessarily in the direct vicinity of a Li.

We hereafter explore Ni^{3+} environments in intermediate Li/vacancy configurations. For the one vacancy (1 Va) local environment (second row in Figure 10), a positive Jahn-Teller distortion is observed whereby the axis comprising the vacancy contracts, consistent with rule 1, while one of the two axes comprising two collinear Li ions elongates and the other contracts.

For a NiO_6 octahedron surrounded by two Li vacancies (2 Va), the resulting Jahn-Teller distortion depends on the vacancy arrangement. When the two vacancies are diametrically opposed, as in Figure 10a, the octahedron contracts along the axis connecting them, consistent with rule 1. The remaining two axes, each flanked by Li ions, expand slightly in accordance with rule 2, yielding an overall negative Jahn-Teller distortion. By contrast, when the vacancies are not directly opposing, as in Figure 10b, the octahedron elongates along the axis defined by the two Li ions. The other two axes, each comprising one vacancy and one Li site, contract in line with rule 3, resulting in a positive Jahn-Teller distortion.

Similar trends are observed for the three vacancy (3 Va) environments. For the configuration shown in Figure 10c, the octahedron elongates along the axis comprising two Li and contracts along the axes containing one and two vacancies, respectively. For the configuration shown in Figure 10d, each cartesian axis comprises a Li and a vacancy, leading to frustration. In this case, no Jahn-Teller distortion can produce compression along all three axes. Instead, the octahedron distorts to maximize compression along vacancy directions, with one axis elongating and the other two contracting, leading to a positive Jahn-Teller distortion.

Jahn-Teller distortions of Ni^{3+} octahedra surrounded by four Li vacancies are more complex. The environment shown in Figure 10h clearly follows rules 1 and 2, with elongation along the axis comprising two Li ions and contraction along the axes containing two vacancies. In contrast, other Li/vacancy arrangements give rise to structural frustration, producing a variety of octahedral distortions, as illustrated in Figure 10e-g. In all cases, the octahedron contracts along the axis comprising two vacancies (rule 1), while the remaining axes may contract, expand or remain nearly unchanged, resulting in positive, negative or mixed Jahn-Teller distortions. Although not every vacancy axis is compressed, at minimum, compressions occur along half of the vacancy-containing axes.

Finally, NiO_6 octahedra surrounded by 5 Va do not appear to be Jahn-Teller distorted in any of our calculations Figure 10.

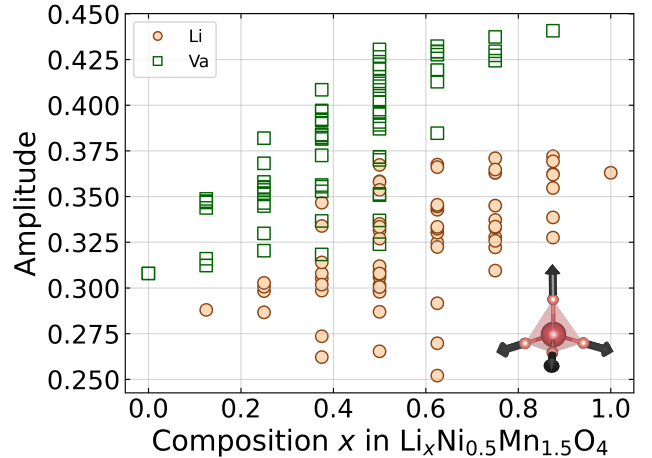


Figure 11: Breathing mode amplitudes of Li tetrahedra in ferrimagnetic LNMO, labeled according to site occupation (Li, Va). Green squares and beige circles depict the amplitudes of vacant and occupied Li sites, respectively.

The above analysis indicates that compressions preferentially occur along axes containing at least one Li vacancy, primarily due to elastic interactions between the NiO_6 octahedron and the surrounding lattice. Contraction along a given axis stretches the neighboring Li tetrahedron sharing a bridging oxygen. The breathing mode amplitudes of tetrahedral Li sites in $\text{Li}_x\text{Ni}_{0.5}\text{Mn}_{1.5}\text{O}_4$ as a function of Li composition are shown in Fig-

ure 11. Overall, vacant Li sites expand more than occupied ones, likely reflecting the impact of bonding and electrostatic interactions on constraining the Li–O interatomic distance. This explains why NiO_6 octahedra more easily contract along axes containing vacant Li sites than along axes with occupied sites.

Finally, the transition metal octahedra in LNMO also exhibit pinching distortion modes (Figure 6c). Transition metal ordering over the octahedral interstices formed by the face-centered cubic oxygen framework breaks the local cubic symmetry, enabling those pinching distortions of the octahedra. The magnitude of this distortion mode ($\sqrt{q_4^2 + q_5^2 + q_6^2}$) is strongly dependent on the transition metal type (Ni, Mn) and oxidation state, as is evident in Figure 12a. Distortion amplitudes in the full three-dimensional q_4 - q_5 - q_6 space are shown in Figure 12b. In this space, each octahedral distortion has an amplitude vector that combines all three pinching modes in equal amounts (*i.e.*, $q_4=q_5=q_6$). This in turn generates a rhombohedral distortion of the cubic octahedron, resulting in a compression (or expansion) of two opposing faces of the octahedron. The four symmetrically equivalent rhombohedral distortions of an octahedron have amplitudes that form a tetrahedron in q_4 - q_5 - q_6 space. Figure 12 shows that the NiO_6 octahedra exhibit large rhombohedral distortions in the fully lithiated $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ spinel, where Ni has a formal oxidation state of +2. Similar to the breathing modes, distinct Ni bands appear, corresponding to each Ni oxidation state, showing that the degree of rhombohedral distortion of NiO_6 octahedra decreases as Ni is oxidized during Li extraction. Conversely, the degree of rhombohedral distortion of MnO_6 octahedra increases slightly upon charging (even though Mn remains 4+), but the overall increase in distortion amplitude is smaller than that observed for the NiO_6 octahedra.

3.3 The effect of Li hops on Jahn-Teller distortions

The strong dependence of the nature and orientation of a Jahn-Teller distorted NiO_6 octahedron on its surrounding Li/vacancy ordering has consequences for Li diffusion. A Li hop from a tetrahe-

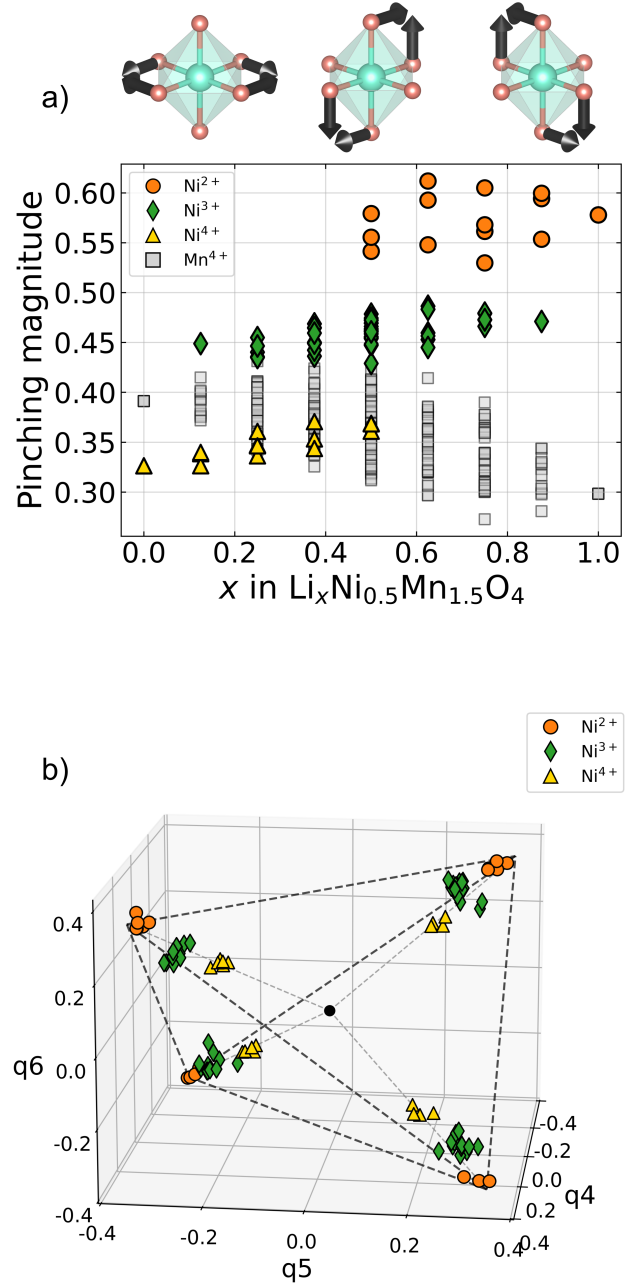


Figure 12: (a) Pinching mode amplitude magnitudes of the ferrimagnetic configurations of $P4_332$ LNMO. (b) Distortion amplitudes of the pinching mode in the full three-dimensional q_4 - q_5 - q_6 space for each Ni octahedron in LNMO, labeled by oxidation state.

dral site to a neighboring vacant tetrahedral site will result in a change in the local Li/vacancy arrangement of surrounding NiO_6 octahedra. The initial orientation of a Jahn-Teller distorted NiO_6 octahedron may no longer be favored after the Li ion has performed a hop. As a result, the Jahn-Teller distorted NiO_6 octahedron will often need to reorient as part of the Li hop.

We explored the reorientation of Jahn-Teller distorted NiO_6 octahedra in response to Li hops by calculating the migration barriers and relaxation paths of three Li-vacancy hops using the Nudge Elastic Band (NEB) method as implemented in Transition State Tools for VASP.^{59–61} The cubic unit cell of $\text{P4}_332 \text{Li}_x\text{Ni}_{0.5}\text{Mn}_{1.5}\text{O}_4$ was used. This supercell contains four Ni cations, 12 Mn cations and 32 oxygen ions.

Figure 13 shows the energy as well as the evolution of the q_2 - q_3 normal mode amplitudes of each NiO_6 octahedron along three different Li hop paths in $\text{Li}_x\text{Ni}_{0.5}\text{Mn}_{1.5}\text{O}_4$. Figure 13(a) shows the energy for a nearest neighbor Li hop in a Li/vacancy configuration at $x = 3/4$. The midpoint of a hop between neighboring tetrahedral sites in spinel is an octahedrally coordinated site.⁶⁹ For this particular hop, the octahedral site is a saddle point (maximum along the hop coordinate) (Figure 13(a)i). As is evident in the q_2 - q_3 plot for this hop (Figure 13(a)ii), two NiO_6 octahedra undergo significant changes in their Jahn-Teller distortion. The octahedron of the green diamond Ni^{3+} gradually deforms from a positive Jahn-Teller distortion, elongated along the $\hat{z}$ axis of the crystal, to a negative Jahn-Teller distortion, with its short axis aligned along $\hat{x}$. The octahedron of green circle Ni^{3+} simply undergoes a reorientation, with its long axis aligned along $\hat{y}$ in the initial state of the hop and aligned along $\hat{z}$ in the end state of the hop. Figure 13(a)ii shows that the reorientation of the green circle Ni^{3+} octahedron occurs abruptly around the midpoint of the Li hop, as is evident by the large discrete jump in the path traversed by the green circles in the q_2 - q_3 plot.

Figure 13 (b) shows similar behavior for a different Li hop in a Li/vacancy configuration again at $x = 3/4$. The energy along this hop exhibits a local minimum when Li passes through the intermediate octahedral site (Figure 13(b)i).

The Jahn-Teller distortions of two NiO_6 octahedra again undergo significant changes along the Li hop (Figure 13(b)ii). The octahedron surrounding the green circle Ni^{3+} starts with a negative Jahn-Teller distortion with its short axis aligned along $\hat{x}$ and ends with a positive Jahn-Teller distortion with its long axis aligned along the $\hat{y}$ axis. The Jahn-Teller distortion of the green diamond Ni^{3+} , in contrast, simply reorients with its long axis initially aligned along $\hat{y}$, but ending up aligned along $\hat{x}$ after the hop. Similar to the green circle Ni^{3+} in part (a)ii, the green diamond Ni^{3+} in part (b)ii undergoes an abrupt reorientation around the midpoint of the Li hop.

The third example in Figure 13(c) is for a hop in a Li/vacancy configuration at $x = 5/8$; its energy is shown in Figure 13(c)i. Figure 13(c)ii shows that the rearrangement of the Jahn-Teller distorted NiO_6 octahedra are less severe than the two other examples, with only the green diamond Ni^{3+} octahedron deforming from a negative Jahn-Teller distortion along the $\hat{x}$ direction to a positive Jahn-Teller distortion along the $\hat{y}$ direction.

The three examples of Figure 13 show that large structural deformations involving qualitative changes in the nature of Jahn-Teller distortions and the orientation of Jahn-Teller distortions accompany Li hops within spinel $\text{Li}_x\text{Ni}_{0.5}\text{Mn}_{1.5}\text{O}_4$. Structural rearrangements of this nature require large ionic displacements not only of the migrating Li ion, but also of the surrounding oxygen ions.

4 Discussion

Understanding redox processes in insertion compounds is crucial for the design and optimization of electrode materials for Li- and Na-ion batteries. The nature, extent, and reversibility of these redox processes determine both the theoretical capacity and the thermodynamic stability of the crystal structure following charge transfer. Transition metal oxides remain the most commercially-relevant and extensively studied intercalation compounds. Although formal oxidation states are often assigned to the constituent ions, the underlying redox mechanisms are better described in terms of molecular or-

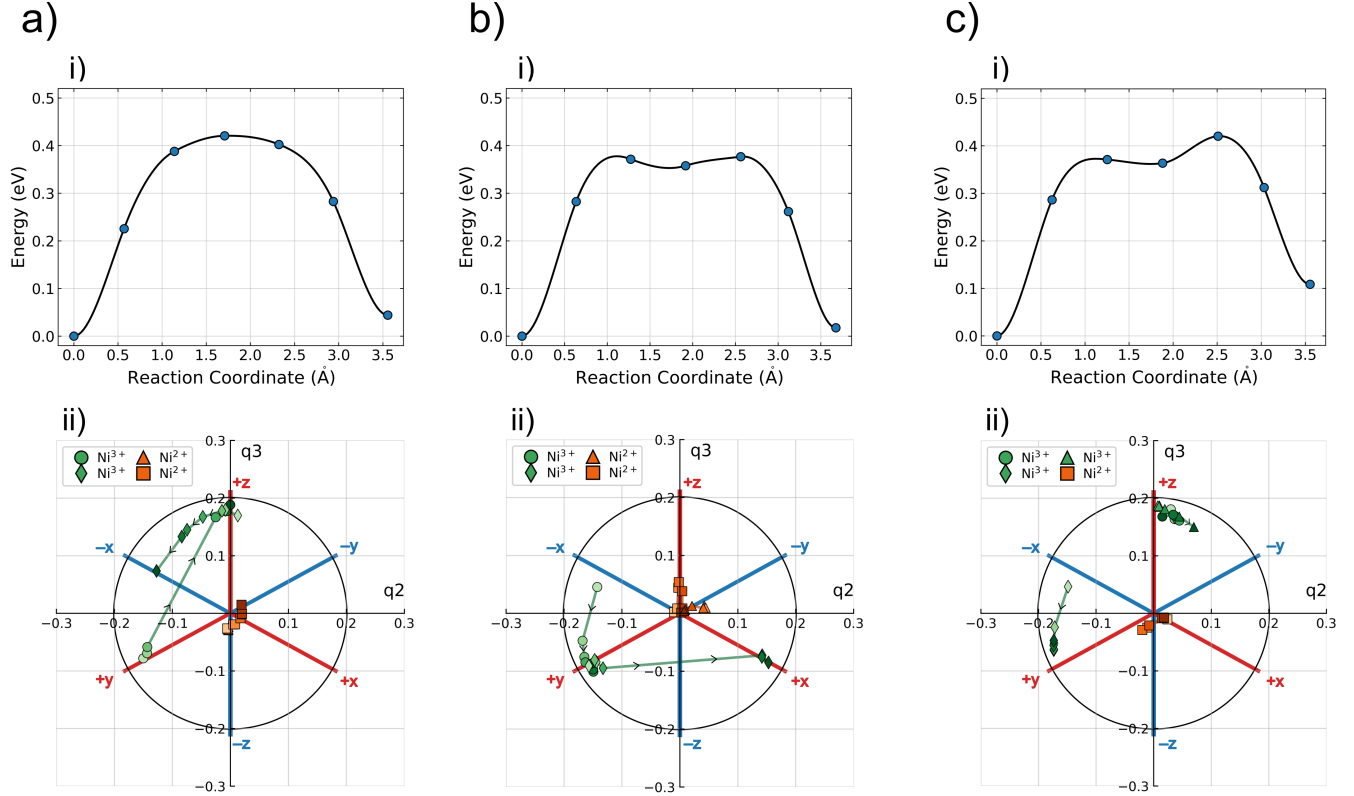


Figure 13: Three examples of nearest-neighbor tetrahedral Li-Li hops in $\text{Li}_x\text{Ni}_{0.5}\text{Mn}_{1.5}\text{O}_4$ at (a) $x = 3/4$ (b) $x = 3/4$ and (c) $x = 5/8$. (a)i, (b)i, (c)i show the energy barriers for each hop as calculated with the NEB method. (a)ii, (b)ii, and (c)ii show the q_2 - q_3 Ni octahedral distortions for each hop NEB image. All final octahedral q_2 - q_3 distortions follow the rules described in Figure 9. For each Ni octahedron shown on the plots, the lightest (darkest) shades represent the initial (final) NEB endpoints.

bitals arising from hybridization of atomic orbitals within TMO_x polyhedral units of the crystal. Layered and spinel cathode materials comprise TMO_6 octahedra as elementary building blocks. Taking the example of a NiO_6 octahedron, e_g^* anti-bonding molecular orbitals, formed from hybridization of the Ni d_{z^2} or $d_{x^2-y^2}$ orbitals with six O p orbitals (Figures 4(a) and (b)), enable $\text{Ni}^{2+}/\text{Ni}^{3+}/\text{Ni}^{4+}$ redox. Other examples of solid-state redox processes that involve molecular orbitals include S-S dimer formation in anion redox sulfides,^{70–72} the π redox process proposed for the $\text{Na}_2\text{Mn}_3\text{O}_7$ cathode,²⁷ which involves hybridized six-membered $\text{Mn}_6\text{-O}_6$ rings, and metal-metal bonded clusters in early transition metal oxides.^{66,73–77} In this sense, it is often misleading to ascribe a redox process in a solid as occurring on an isolated ion, whether it is a transition metal cation or an oxygen anion. Such simplification obfuscates the important role that rehybridization plays in the redox process,^{78,79} and fails to elucidate the links between redox processes and their accompanying structural distortions.^{31,66,68,77}

In particular, recent studies have extended the concept of anion redox to Li stoichiometric layered oxide cathodes, such as LiNiO_2 , whose theoretical capacity can otherwise be explained by pure transition metal redox. While several competing mechanisms^{16,23–29} have been proposed to explain anion redox, a widely accepted conception of “pure” anion redox refers to the donation/removal of an electron to/from a localized oxygen orbital. This mechanism has been invoked to explain anomalous capacity in Li-excess electrodes containing “orphan” oxygen p orbitals.^{13,14} A recent study²¹ argued that a similar mechanism occurs in LiNiO_2 at high states of charge based on a Bader charge analysis that showed charge depletion on oxygen upon extraction of Li, even though all O are bonded to three Ni atoms in this structure. However, a holistic approach that draws on a range of metrics, including not only Bader charges but also local magnetic moments, charge difference plots, and structural distortions, is necessary to develop an accurate understanding of redox processes.

To study Ni redox and its structural consequences in transition metal oxides, we have focused here on the spinel $\text{Li}_x\text{Ni}_{0.5}\text{Mn}_{1.5}\text{O}_4$ com-

pound with the cation-ordered $P4_332$ structure. In this compound, redox activity is associated with the e_g^* electronic levels of NiO_6 clusters that are geometrically isolated in the spinel crystal structure, sharing edges exclusively with redox-inactive MnO_6 octahedra. As a result, redox is expected to be largely localized, with structural distortions induced by redox activity and Jahn-Teller instabilities being elastically shielded from each other. Using a variety of methods to analyze redox, we find that even in this relatively simple and supposedly well understood oxide cathode, redox reactions and their structural consequences are complex and subtle. Analysis of magnetic moments, inferred from the number of unpaired valence electrons of each ion, indicates that electronic changes with Li content occur exclusively on the Ni cations. However, Bader charge analysis shows instead that local charge densities change not only on Ni but also on oxygen. Charge difference plots, obtained by subtracting the electronic charge density computed before and after removal of one Li atom from the unit cell (from $x = \frac{1}{8}$ to $x = 0$), while keeping all structural parameters fixed, reveal clear changes in the electronic distribution around both Ni-O and Mn-O bonds.

The charge difference plots indicate that redox activity on Ni leads to a rehybridization of the σ -type e_g^b bonds between Ni and O, converting an initially more covalent bond to a more ionic bond by displacing charge from the Ni towards the oxygen. Although polarization of the Ni-O bond increases the oxygen charge, as confirmed by Bader charge analysis, it should not be interpreted as anion redox. Instead, it represents a secondary consequence of electron transfer involving the expected NiO_6 e_g^* states. As shown in Figure S6, the changes in the Bader charges on the oxygen ions in $\text{Li}_x\text{Ni}_{0.5}\text{Mn}_{1.5}\text{O}_4$ upon Li extraction are comparable to those reported for oxygen in layered Li_xNiO_2 .²¹ Furthermore, redox-induced rehybridization processes have been reported in Li_xCoO_2 ,^{78,79} and preliminary charge difference analysis of $\text{Li}_{1/8}\text{NiO}_2$ suggests that redox processes likewise induce rehybridization in this material (Figure S7).

Surprisingly, rehybridization of the Ni-O e_g^b bonds in $\text{Li}_x\text{Ni}_{0.5}\text{Mn}_{1.5}\text{O}_4$ has a ripple effect that extends beyond the NiO_6 octahedron itself and

causes the neighboring Mn-O bonds to rehybridize as well. Charge accumulation on oxygen during redox involving the NiO_6 e_g^* states weakens the Mn-O e_g^b bond, which is compensated by strengthened π bonding between Mn t_{2g} orbitals and O p orbitals. Even though Mn is redox inactive in the sense that its magnetic moment and excess Bader charge do not change with Li concentration, there is non-negligible charge reorganization around the Mn cations.

Redox processes often have structural consequences, including collective distortions of the ion cluster that hosts the redox-active molecular orbitals. In $\text{Li}_x\text{Ni}_{0.5}\text{Mn}_{1.5}\text{O}_4$, redox on the NiO_6 octahedra results in several symmetrically-distinct collective distortions. First, NiO_6 octahedra increase in volume as the Ni formal oxidation state changes from Ni^{4+} to Ni^{3+} to Ni^{2+} . This volumetric evolution indicates that redox not only involves the transition metal d states but the electronic energy levels of the NiO_6 octahedra as a whole. The NiO_6 octahedra are also Jahn-Teller active when Ni has a formal oxidation state of 3+. Since the NiO_6 octahedra in LNMO are isolated from one another, their Jahn-Teller active distortions can adopt relatively unconstrained orientations. Our results demonstrate a strong coupling between the nature and orientation of NiO_6 Jahn-Teller distortions and their local Li/vacancy environment. While similar couplings to specific Li- or Na-vacancy orderings has been reported in layered intercalation compounds,^{46,80} in spinels this interaction appears to be primarily driven by strain-energy minimization. Such coupling has implications for Li diffusion, since a Li hop will necessarily result in a change in the local Li/vacancy environment around a Jahn-Teller distorted NiO_6 octahedron. As Li migrates, the Jahn-Teller distortions of neighboring NiO_6 octahedra often need to reorient to accommodate changes in the local Li/vacancy ordering. Such reorientation requires sizable vibrational excitations to enable the hop, and future work should explore the consequences of these large structural rearrangements on the vibrational prefactors appearing in transition-state-theory expressions for hop frequencies.⁸¹

A surprising prediction of this work is the significant impact of the Ni oxidation state on the

extent of rhombohedral distortion of the NiO_6 octahedra (Figure 12). As mentioned in Section 3.2, when all three pinching modes, q_4 , q_5 and q_6 , (Figure 6(c)) are active with equal magnitude, an overall rhombohedral distortion is observed with the compression of two opposing triangular faces of the cubic reference octahedron. The same distortion occurs in layered compounds with $R\bar{3}m$ symmetry such as LiCoO_2 and LiNiO_2 .³⁰ We attribute the strong dependence of the rhombohedral distortion amplitude on Ni oxidation state to a change in Ni-O covalence as a result of redox. As revealed by the charge difference plots and Bader charge analysis, the Ni-O bonds become less polarized, and therefore more covalent, with increasing Ni oxidation state. It is possible that an increase in covalence strengthens directional bonding, decreasing the tolerance for symmetry-breaking rhombohedral distortions of the cubic reference octahedron.

The localized structure descriptors used in this work to analyze redox states and their structural consequences are ideally suited for a compound such as spinel $\text{Li}_x\text{Ni}_{0.5}\text{Mn}_{1.5}\text{O}_4$, with isolated NiO_6 redox-active octahedra. While such localization facilitates the identification of redox mechanisms and their coupling to local distortions, it can also influence charge transport. Charge transport in systems with isolated redox centers is more likely to occur through thermally activated polaron hopping, whereas more interconnected redox centers can support increasingly delocalized and itinerant charge carriers.^{30,31} We expect that similar descriptors will also help elucidate redox mechanisms in compounds where electronic states are more likely to delocalize, such as layered Li_xNiO_2 , which has edge-sharing redox-active octahedra. The nature of the Jahn-Teller distortions in LiNiO_2 , where Ni has a formal oxidation state of +3, is not well understood.^{33,35,37,68,82,83} Generally, whether Jahn-Teller distortions organize in a cooperative manner or adopt disordered orientations in a non-cooperative manner is temperature dependent, with the transition temperature sensitive to the elastic stiffness of the host crystal structure.³³ An open question is whether localized Jahn-Teller distortions persist upon the removal of Li from Li_xNiO_2 , when only a subset of the Ni cations

are susceptible to Jahn-Teller distortions. The strong dependence of rhombohedral distortions on Ni oxidation state found in $\text{Li}_x\text{Ni}_{0.5}\text{Mn}_{1.5}\text{O}_4$ also raises the question as to whether similar local variations in the degree of rhombohedral distortion can be sustained in compounds with more interconnected redox centers such as layered Li_xNiO_2 .

Experimental validation is valuable for establishing the physical relevance of our computational predictions; however, directly confirming the mechanisms identified in this work remains challenging. The present study focuses on the redox processes in LNMO and their relationship to specific local environments. Our results support a rehybridization-based description of the redox processes involving changes in the electronic states of Ni, O, and Mn species. Although spectroscopic techniques such as X-ray absorption spectroscopy (XAS) can provide important insights into element-specific redox activity, validating such a rehybridization argument requires information from all species participating in the electronic charge redistribution. In practice, this necessitates multiple experimental probes, with different sensitivities and probing depths. In LNMO, for example, the transition metals Ni and Mn are commonly investigated using hard X-ray techniques,^{84,85} whereas oxygen is typically probed using soft X-rays with a significantly lower probing depth.⁸⁶ Consequently, constructing a unified experimental picture of the electronic changes occurring during redox is challenging. Furthermore, while XAS provides valuable information regarding redox processes, the interpretation of spectral features often requires careful analysis as the definitive assignment of the spectral evolution to a specific redox process can only be achieved through comparison of the experimental data with first-principles predictions for different redox scenarios.^{87,88}

Similarly, challenges arise when attempting to experimentally validate the local structural distortions identified in this work. Techniques such as extended X-ray absorption fine structure (EXAFS) and nuclear magnetic resonance (NMR) probe the local structure. However, NMR cannot be directly applied to Ni due to the low abundance and sensitivity of its NMR active iso-

tope (^{61}Ni), and is not applicable to paramagnetic species, including Mn^{3+} and Mn^{4+} . Meanwhile, $^6\text{Li}/^7\text{Li}$ NMR typically leads to at least partial signal averaging due to rapid Li-ion motion on the NMR timescale.^{89–91} The interpretation of ^{17}O NMR data for paramagnetic cathodes remains too challenging to be useful at this time. EXAFS can provide valuable information regarding local bonding and distortions around Ni; however, extensive signal overlap and the absence of information on Li positions make it impossible to isolate and characterize the individual local configurations predicted by first principles methods. In this context, this work provides a complementary local electronic-structure perspective that can help disentangle the contributions of individual local environments that are difficult to isolate experimentally.

Beyond the bulk redox processes examined here, surface and interfacial processes are also important considerations in high-voltage cathode materials. The mechanisms identified here are intended to describe the intrinsic bulk thermodynamic behavior of $\text{Li}_x\text{Ni}_{0.5}\text{Mn}_{1.5}\text{O}_4$ and do not explicitly account for surface reconstruction, oxygen loss, or electrolyte-driven interfacial reactions during cycling. The $\text{Li}_x\text{Ni}_{0.5}\text{Mn}_{1.5}\text{O}_4$ spinel has a high open-circuit voltage, where electrolytes become susceptible to decomposition reactions. This can result in oxygen loss and electrolyte-driven interfacial reactions during cycling.^{92–94} Nevertheless, the results of this study remain directly relevant for understanding the bulk behavior of the $\text{Li}_x\text{Ni}_{0.5}\text{Mn}_{1.5}\text{O}_4$ spinel. For large electrode particles, bulk properties dominate the electrochemical response, whereas nanoscale particles have a larger surface area to volume ratio and, at sufficiently small particle sizes, surface phenomena can dominate the electrochemical response.

First-principles predictions of phase stability, redox mechanisms and electrochemical properties are sensitive to the approximation to density functional theory and any semi-empirical extensions to treat highly correlated electronic states. Furthermore, it is often difficult to account for low concentration defects in first-principles calculations. For example, a barrier to understanding fundamental properties of Li_xNiO_2 is the presence

of excess Ni within the Li layer in experimental samples, which is rarely accounted for in theoretical studies. Hence, it is unclear whether disagreements between calculated and experimental voltage profiles of a material such as Li_xNiO_2 are due to the effect of excess Ni in the Li layer or due to fundamental shortcomings of DFT and its extensions. It is well known that the degree of electron localization can be controlled by empirically modifying the Hubbard U parameters in DFT+ U calculations. In our study of $\text{Li}_x\text{Ni}_{0.5}\text{Mn}_{1.5}\text{O}_4$, we relied on $r^2\text{SCAN}$ without an explicit Hubbard U correction, which was shown to be remarkably accurate in describing magnetic interactions between Ni and Mn in $\text{Li}_x\text{Ni}_{0.5}\text{Mn}_{1.5}\text{O}_4$ as validated by a comparison of predicted magnetic transition temperatures to experimentally measured values.⁶⁴

In this work, we primarily focused on the well-ordered $P4_332$ $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ spinel compound. However, spinel compounds with the same composition used in commercial batteries exhibit a significant degree of disorder among the Ni and Mn cations over the TM sites of the spinel crystal structure. Nevertheless, we expect that many of the predictions made for $P4_332$ $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ should transfer to more disordered spinels. Even when Ni and Mn are disordered, their arrangement is not random, but preserves some degree of short-range order that is similar to that exhibited by the long-range ordered $P4_332$ structure. A first-principles study of over 40 Ni-Mn orderings in $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ spinel predicted that Ni prefers to be surrounded by Mn and that configurations hosting edge-sharing NiO_6 - NiO_6 octahedra consistently have higher energies relative to those configurations that do not, including the $P4_332$ ground state ordering.⁶⁴ Hence, similar to $P4_332$, the majority of Ni in the disordered spinels are likely surrounded by Mn octahedra. Redox and Jahn-Teller distortions will then also occur on isolated NiO_6 octahedra that are elastically shielded from each other by intervening MnO_6 octahedra in spinels with Ni-Mn disorder.

Finally, our analysis of redox mechanisms, their structural consequences, and their dependence on local Li/vacancy orderings sets the stage for a statistical mechanics study of finite temperature electrochemical properties⁹⁵ of complex electrode materials such as $\text{Li}_x\text{Ni}_{0.5}\text{Mn}_{1.5}\text{O}_4$ and lay-

ered $\text{Li}_x\text{Ni}_y\text{Mn}_z\text{Co}_{1-y-z}\text{O}_2$ (*i.e.*, NMC). The electrochemical properties of these electrode materials depend sensitively on the coupling between multiple chemical and electronic degrees of freedom, including Li-vacancy disorder, localized heterogeneity in oxidation states, magnetic disorder, and non-cooperative Jahn-Teller distortions. At finite temperature, these degrees of freedom generate entropy and affect the mechanisms of collective ion transport.^{95,96} Cluster expansion surrogate models^{52,97-105} that describe the energy of the crystal as a function of the chemical, structural, and electronic degrees of freedom can interpolate and generalize first-principles electronic structure calculations within Monte Carlo simulations where excitations are explicitly sampled and thermodynamic and kinetic properties are calculated. This will be the focus of future work.

5 Conclusion

In this work, we investigated the redox behavior and local structural evolution associated with Li (de)intercalation in the cation-ordered $P4_332$ $\text{Li}_x\text{Ni}_{0.5}\text{Mn}_{1.5}\text{O}_4$ spinel. By combining magnetic-moment analysis, Bader charge calculations, and charge-density difference maps, we found that redox occurs exclusively on Ni, while also inducing apparent rehybridization of both Ni-O and Mn-O bonds. Consequently, changes in oxygen charge are better interpreted as polarization effects associated with Ni-centered e_g^* redox rather than evidence of true anion redox. Rehybridization of Ni-O σ bonds propagates to neighboring MnO_6 octahedra, redistributing charge between the Mn t_{2g} and e_g manifolds, even though Mn remains formally redox inactive.

Redox activity on Ni also leads to characteristic polyhedral distortions: NiO_6 octahedra expand volumetrically upon reduction and exhibit Jahn-Teller distortions in the Ni^{3+} state. The orientation of these distortions is tightly coupled to the local Li/vacancy environment, following clear geometric rules that favor compression along axes adjacent to Li vacancies. We also observe pinching modes in both NiO_6 and MnO_6 octahedra that vary systematically across different states of charge.

Collectively, these results clarify how electronic and structural degrees of freedom interact during (de)lithiation in this ordered spinel and highlight underlying factors—such as local Li/vacancy environments and transition metal-oxygen rehybridization—that shape the behavior of this cathode. These insights may help inform the interpretation and prediction of redox-structure coupling in more complex transition-metal oxide cathodes.

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