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Structural Characterization of the Li-Ion Battery Cathode Materials 
LiTi$_x$Mn$_{2-x}$O$_4$ (0.2 ≤ x ≤ 1.5): A Combined Experimental $^7$Li NMR and First-Principles Study

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Supporting Information

ABSTRACT: Titanium doping in lithium manganese oxide spinels was shown to be beneficial for the structural stability of the potential Li-ion battery cathode materials LiTi$_x$Mn$_{2-x}$O$_4$, 0.2 ≤ x ≤ 1.5, yet the distribution of Li/Ti/Mn in the structure and the cation oxidation states, both pivotal for the electrochemical performance of the material, are not fully understood. Our work investigates the changes in the local ordering of the ions throughout this series by using a combination of $^7$Li NMR spectroscopy and ab initio density functional theory calculations. The $^7$Li NMR shifts are first calculated for a variety of Li configurations with different numbers and arrangements of Mn ions in the first metal coordination shell and then decomposed into Li−O−Mn bond pathway contributions to the shift. These Li−O−Mn bond pathways are then used to simulate and assign the experimental NMR spectra of different configurations and stoichiometries beyond those in the initial subset of configurations via a random distribution model and a reverse Monte Carlo approach. This methodology enables a detailed understanding of the experimental $^7$Li NMR spectra, allowing the variations in the local ordering of the ions in the structure to be identified. A random distribution of Ti$^{4+}$−Mn$^{3+/4+}$ sites is found at low Ti content (x = 0.2); an inhomogeneous lattice of Mn$^{3+}$-rich and Ti$^{4+}$-rich domains is identified for x = 0.4, and single-phase solid solution is observed for x = 0.6 and 0.8. A mixed Li−Mn$^{2+}$ tetrahedral and Li−Mn$^{3+/4+}$−Ti octahedral configuration is determined for the x = 1.0 case. A specific cation ordering in the partially inverse LiTi$_{1/2}$Mn$_{1/2}$O$_4$ case is found, which transforms into a two-phase network of disordered Mn$^{3+}$-rich and ordered Mn$^{2+}$-rich domains for x = 1.1−1.4.

INTRODUCTION

Spinel-type lithium metal oxides are interesting cathode materials for rechargeable Li-ion battery applications. The robust host structure of spinel oxides retains capacity for many cycles, and the three-dimensional network of interstitial sites allows high Li diffusion rates.1,2 LiMn$_2$O$_4$ spinel has been studied as a potential alternative to the more widely used LiCoO$_2$ because of its lower cost, lower toxicity, and higher thermal stability.2,3 However, the application of Li$_x$Mn$_2$O$_4$ as a positive electrode is limited by the presence of Jahn−Teller active Mn$^{4+}$ ions, which accelerate structural degradation of the material upon cycling due to a cooperative Jahn−Teller distortion.4 Moreover, the charge disproportionation of 2Mn$^{3+}$ −→ Mn$^{4+}$ + Mn$^{2+}$ results in the formation of Mn$^{2+}$ ions, which dissolve in the electrolyte at the surface of the particles and deplete the spinel framework of transition-metal ions.5 The electrochemical properties and the structural stability of LiMn$_2$O$_4$ were shown to be improved by introducing excess Li in the spinel structure to form Li$_{1+x}$Mn$_{2−x}$O$_4$.6−8 The inclusion of the excess lithium raises the average Mn oxidation state, thereby reducing the amount of Jahn−Teller active Mn$^{3+}$ ions. Another approach to limit the negative effects of the cooperative Jahn−Teller distortion has been to partially substitute the Mn ion with other transition metals (TM) such as Ni, Zn, and Ti, hence stabilizing the structural integrity of the electrode upon cycling.10−13 Under-
standing the structural ordering and the distribution of Li/TM ions in the structure is central to rationalizing the relationship between the electrochemical performance and the physical properties of the material. As an example, the kinetic and electrochemical properties of the high-energy LiNiMn_{2−x}O_{4} cathode material have been analyzed in relation to the complex cation ordering throughout the series, unraveling the key role of compositional (dis)order in the electrochemical performance of this material.15,16 Here, the randomization of Ni/Mn ions among the octahedral sites of the spinel lattice was proposed to lead to improved electrochemical performance.

In this work, we focus on the series of materials Li(Ti)xMn_{2−x}O_{4} with 0.2 ≤ x ≤ 1.5 and study the structural changes of the Mn-oxide spinel framework as an effect of Ti doping. In spinel materials of general formula AB₂O₄, the oxygen anions form a face-centered-cubic sublattice, within which octahedral (Oh) and tetrahedral (Td) interstitial sites are present in a 2:1 ratio. In a normal spinel, the A cations occupy the Td sites, and the B cations occupy the Oh sites (denoted as A[AB₂]O₄), while in an inverse spinel, the B cations occupy all of the Td sites and half of the Oh sites, and the A cations occupy the other half of the Oh sites (denoted as B[AB₂]O₄). In the case of LiTiₓMn_{2−x}O_{4}, the partial substitution of Mn with Ti results in a mixed cation occupancy on both the Oh and Td sites of the spinel lattice.15,16 In the LiTiₓMn_{2−x}O_{4} series for 0.2 ≤ x ≤ 1.0, the disordered Fd̅3m cubic spinel preferentially forms (Figure 1a) with proposed partial occupancy of Li⁺/Mn³⁺ and Li⁺/Ti⁴⁺/Mn³⁺⁴⁺ on the tetrahedral 8a and the octahedral 16d sites, respectively, and with the Li(Oh)/Mn³⁺(Td) fraction increasing with increasing Ti content. For x > 1.0, the more ordered P4₃3₂ (b) space group with the A and B cations shown in purple spheres and the oxygens shown in red spheres. The crystallographically independent octahedral and tetrahedral sites are represented by polyhedra of different colors as labeled. Based on X-ray diffraction (XRD) showed limited accuracy in determining the distribution of Li, Ti, and Mn ions in the lattice due to the difficulty of detecting Li in the presence of heavier elements and of distinguishing between Ti and Mn, which have similar X-ray scattering factors.15,16 Electron spin resonance (ESR) studies were also used in combination with XRD analysis, but the presence of multiple Mn oxidation states made the assignment of the TM distribution challenging.16

⁶⁷Li NMR has been successfully used to characterize the local Li environments and the cation ordering in similar systems such as LiMn₂O₄, LiZnMn₂−xO₄, and LiNiMn₂−xO₄ as well as in Li-excess Mn oxides, Liₓ,Mn₂−xO₄. The dominant interaction leading to the observed ⁶⁷Li NMR shift in this class of paramagnetic materials is the isotropic Fermi contact (FC) hyperfine interaction, which results from the coupling between the nuclear moment of the Li and the time-average of the local field due to the unpaired d electrons present on the neighboring TM ions.19,26 In the series of systems studied here, Ti is present as Ti⁴⁺ throughout (i.e., d⁰ ion); hence, the only paramagnetic centers are the Mn²⁺/³⁺/⁴⁺ sites (i.e., d⁰/d⁵⁻/⁷⁻ ions, respectively). The Fermi contact interaction is proportional to the unpaired spin density transferred from the d orbitals of Mn to the s orbitals of Li. This transfer can occur either directly through the overlap of the involved orbitals or, more prominently in the systems studied here, indirectly via the bridging oxygen p orbitals which form Mn=O–Li bond pathways. The observed ⁶⁷Li Fermi contact shift is hence given by the sum of the individual Mn–O–Li pathway contributions.25 The sign and magnitude of the shift depend on the geometry and covalency of the pathway as well as on the Mn oxidation state and on the magnetic susceptibility of the material. In mixed cation systems, the variety of Li environments often results in a multitude of paramagnetic shifts and a significant broadening of the resonances, making the spectra difficult to interpret.30 Computational predictions and ab initio calculations of paramagnetic NMR parameters constitute a robust and invaluable aid for the understanding of experimental NMR spectra of paramagnetic solids.31 The interpretation of the experimental spectra is supported by first-principles density functional theory (DFT) calculations of the magnetic interactions

Figure 1. Polyhedral representation of a general spinel-type AB₂O₄ in the Fd̅3m (a) and P4₃3₂ (b) space group with the A and B cations shown in purple spheres and the oxygens shown in red spheres. The crystallographically independent octahedral and tetrahedral sites are represented by polyhedra of different colors as labeled.
and 7Li NMR shifts. Different LiTi Mn$_{2−x}$O$_4$ structures of (possibly fictitious) ferromagnetically aligned TM ions are simulated, from which we calculate the Mn−O−Li bond pathway contributions to the 7Li hyperfine shift of the various environments, nominally at 0 K. To compare these shifts with the experimental spectra obtained at infinite temperature, we evaluate the possible Mn−Mn magnetic interactions, determine the Curie−Weiss magnetic factors, and use these to scale the shifts obtained with density functional theory (DFT) to the paramagnetic regime of the NMR experiments (performed at room temperature). The library of bond pathway contributions are subsequently used to simulate the spectra of different LiTi Mn$_{2−x}$O$_4$ configurations in a combined random distribution model and reverse Monte Carlo approach, allowing the characterization of the cation ordering throughout the series. A random distribution of Ti$^{4+}$−Mn$^{3+}$/4$^+$ sites among the octahedral 16d environments (Fd$ar{3}$m) is found at low Ti content ($x = 0.2$), which transforms into a lattice of Mn$^{3+}$−rich and Mn$^{4+}$−rich phases for $x = 0.4$ and a single-phase solid solution for $x = 0.6$ and 0.8. A partially inverse spinel configuration is identified for $x = 1.0$ with mixed Li−Mn$^{2+}$ tetrahedral sites and mixed Li−Mn$^{3+}$/4$^+$−Ti octahedral sites. A specific ion configuration is identified for the LiTi Mn$_{35/8}$O$_4$ case, involving ordering between the tetrahedral 8c and the octahedral 4b and 12d sites in the P4$_{3}$2 lattice, corresponding to (Li$_{0.45}$Ti$_{0.55}$O$_{2.95}$(Li$_{0.56}$Mn$_{0.44}$)$_{0.6}$O$_{1.4}$. This further transforms into a network of Mn$^{3+}$−rich disordered Fd$ar{3}$m and Mn$^{2+}$−rich ordered P4$_{3}$2 domains for the $x = 1.1$−1.4 series.

### EXPERIMENTAL METHODS

#### Synthesis of LiTi Mn$_{2−x}$O$_4$ (0.2 ≤ $x$ ≤ 1.5)

LiTi Mn$_{2−x}$O$_4$ samples ($x = 0.2, 0.4, 0.6, 0.8, 1.0, 1.1, 1.2, 1.3, 1.4, and 1.5$) were prepared via the solid-state synthesis method presented in detail in ref 17. Details of the synthetic procedure are described in the Supporting Information. Table S1 in the Supporting Information summarizes the content of Mn$^{2+}$−rich ordered LiTi Mn$_{2−x}$O$_4$ samples ($x = 0.2, 0.4, 0.6, 0.8, 1.0, 1.2, 1.3, 1.4, and 1.5$) reported in previous XRD studies. 16

#### Solid-State MAS 7Li NMR

Solid-state NMR spectra of the LiTi Mn$_{2−x}$O$_4$ samples ($0.2 ≤ x ≤ 1.5$) were acquired on a Bruker 200 Avance III spectrometer using a 1.3 mm probe with a MAS frequency of 60 kHz. The one-dimensional 7Li spectra were recorded using a double-adiabatic spin−echo sequence, 18 employing a pair of 50 μs tanh/tan short high-powered adiabatic pulses (SHAPs) of 5 MHz sweep width, 54,55 and a 1.025 μs 90° excitation pulse. All pulses used a radiofrequency (RF) field strength of 244 kHz. For each spectrum, 32 768 scans were acquired using a recycle delay of 30 ms. The experimental 7Li NMR spectra were fitted using the DmFit software. 36 An initial model was set up with components based on the hyperfine shifts predicted with DFT calculations, and the fitting of the isotropic region and the sideband pattern was then obtained by optimizing the shift and the amplitude of the deconvoluting regions.

### COMPUTATIONAL METHODS

#### Formation Energies and Thermodynamical Phase Stability

Methodology of Thermodynamical Phase Stability Analysis. The thermodynamical phase stability of the LiTi Mn$_{2−x}$O$_4$ series was studied by calculating the formation enthalpy of various structures with different stoichiometries. For LiTiO$_3$ and LiMnO$_2$, crystal structures were obtained from the International Crystal Structure Database (ICSD) and fully relaxed (i.e., both the unit cell parameters and the atomic positions were allowed to vary) using DFT. From the LiTiO$_3$ and LiMnO$_2$, unrelaxed crystal structures, selected intermediate stoichiometries of the LiTi Mn$_{2−x}$O$_4$ series were generated using the Site Occupancy Disorder (SOD) 17 and the Cluster-Assisted Statistical Mechanics (CASM) 39,39 software. Specifically, for $x = 0.5, 1.0$, and 1.5, small cells of 14 atoms were considered, where all possible swaps between Li, Ti, and Mn were enumerated. For the $x = 1.25$ and 1.5 cases, additional configurations were considered: for larger cells of 56 atoms, all configurations were enumerated starting from LiTiO$_3$ and replacing (2−x) Ti ions with Mn ions. Additionally, swaps between Li, Mn, and Ti were allowed to include inverse spinel lattices in the analysis, i.e., networks of mixed Ti−Mn−Li occupancy on both the tetrahedral and the octahedral sites were generated.

#### Details of GGA+U Calculations of Formation Energies

The unit cell parameters and atomic positions of each generated configuration were relaxed with DFT using the PBE 41 spin-polarized generalized gradient approximation (GGA) functional within the VASP code. 42 The projector augmented waves (PAW) 43 method was used with a plane-wave cutoff of 500 eV and an energy tolerance of 10$^{−7}$ eV, resulting in a convergence of the energy of approximately 4 meV/atom. A force tolerance of 10$^{−5}$ eV/Å was used for ionic relaxations, resulting in a convergence of the energy of approximately 4 meV/atom. A force tolerance of 10$^{−3}$ eV/Å was used for ionic relaxations. The electronic energy of each relaxed structure was calculated with a single-point energy minimization. The reciprocal space sampling was performed with a k-point grid of 8 × 8 × 8 points for the smaller cells (14 atoms) and 4 × 4 × 4 points for the larger cells (56 atoms). To correct for the self-interaction error in the GGA formalism, a Hubbard $U$ parameter was included for the Mn ions to treat the 3d correlations. 43 In this work, the approach proposed by Liechtenstein was used, 44 where the Coulomb matrix ($U$) and the exchange matrix ($J$) are combined to give an overall effective value $U_{eff} = U - J$. The value of $J$ was fixed to 1 eV throughout. In a previous study by Wang et al., 45 values of $U_{eff} = 4.5, 4.0$, and 3.5 eV were calculated for Mn$^{2+}$, Mn$^{3+}$, and Mn$^{4+}$ ions, respectively. Because in our systems the Mn ions are present in multiple oxidation states, an average $U_{eff}$ value of 3.9 eV was chosen for all the Mn sites.

#### Paramagnetic Shift Calculations

The calculation of the Fermi contact shift, $\delta_{FC}$ adopted in this work follows the methodology presented by Kim et al., which is summarized here. In this method, the hyperfine coupling constant, $A_{iso}$, is first calculated from the system in the ferromagnetic state nominally at 0 K and then scaled using a Curie−Weiss factor, $\Phi$, to match the paramagnetic regime typical of NMR experiments.

\[ \delta_{FC} = \frac{A_{iso} 10^3 \Phi}{2 h \nu} \]  

(1)

with

\[ A_{iso} = \frac{2}{3} \mu_B \mu_B' \sum g_i \left| h g_i \right|^2 \]  

(2)

and

\[ \Phi = \frac{B_B \mu_B^2}{3k_B T g_S (S - \theta)} \]  

(3)

where $h$ is the Planck constant, $\nu$ is the Larmor frequency, $h g_i \left| h g_i \right|^2$ is the unpaired spin density at the Li nuclear position, $B_B$ is the static magnetic field, $\mu_B$ is the effective electronic magnetic moment, $\mu_B'$ is the Bohr magneton, $S$ is the formal electronic spin of the paramagnetic center(s), $k_B$ is the Boltzmann constant, $g_S$ is the free-electron g-value, $g_i$ is the nuclear g-factor, $T$ is the temperature used in the experiments, here estimated to be 320 K to account for frictional heating due to MAS NMR, and $\theta$ is the Weiss constant. In this work, $\mu_B$ is taken to be the spin-only value of 2$\mu_B \sqrt{S(S + 1)}$. This is considered a good approximation for the class of systems studied here. As an example, in the case of LiMnO$_3$ with an average oxidation state of Mn$^{3.5+}$, $S = 1.75$, and the calculated spin-only value is $\mu_B = 4.39 \mu_B$, in good agreement with the experimental $\mu_B$ range of 4.33–4.36 $\mu_B$ reported by Masquelier et al. 47

#### Methodology for Calculating the Magnetic Parameters $\theta$ and $\Phi$

Values of $\theta$ were obtained ab initio by calculating the magnetic exchange coupling constants, $J$, by a multivariate linear regression of the DFT-calculated energies of systems with different magnetic configurations of coupled spins. More details of the method are
presented in the Supporting Information. The calculations of the various exchange coupling constants were performed on selected structures, i.e., the lowest energy configurations for the LiTiMnO4, LiTiMnO, LiTiMnO4, LiTiMnO4, and LiTiMnO4 stoichiometries, containing networks of Mn2+, Mn3+, Mn4+, and Mn5+ ions, respectively. When equivalent Mn–Mn interactions are present in different lattices, the corresponding J values were found to differ by less than 3%, differences arising from local distortions of the optimized geometries. All of the considered structures containing Mn5+ ions were found to exhibit a cooperative Jahn–Teller distortion.

Methodology of Hyperfine Coupling Constant, \(A_{\text{iso}}\) Calculation.

The isotropic value of the hyperfine tensor \(A_{\text{iso}}\), in eq 2, was calculated with DFT by integrating the unpaired electron spin density, \(\rho(\mathbf{r}_f)\), directly at the Li nuclear position in the ferromagnetic state, which was then scaled to the paramagnetic regime by multiplying it by the scaling factor \(\Phi\) (eq 1).46 The bond pathway decomposition method presented by Middelmiss et al.29 was followed to obtain the Mn–O–Li Fermi contact bond pathway contribution from each Mn ion to the total Li shift using the computed site-specific scaling factor, \(\Phi\).

Details of Hybrid DFT/Hartree–Fock Calculations of Paramagnetic Shifts.

All calculations of magnetic and hyperfine parameters were performed in CRYSTAL09,45 a solid-state DFT code using a Gaussian-type basis set to describe core states accurately. Because of the high dependence of the calculated paramagnetic shifts on the quality of the Gaussian basis sets, two types were utilized: a small basis set for geometry optimizations, and a more extended basis set for hyperfine and magnetic single-point calculations.

Details are given in the Supporting Information. All calculations were performed with hybrid functionals in the spin polarized state. Previous ab initio studies on Li paramagnetic NMR shifts show that values obtained using 20 and 35% Hartree–Fock (HF) exchange provide the upper and lower bounds for the experimental shifts.25,46 Hence, separate calculations were performed with the B3LYP functional with 20% HF exchange49 (denoted HYB20) and a modified B3LYP with 35% of HF exchange (denoted HYB35). The convergence of the energy and the spin density were checked with respect to the number of sampled points in the reciprocal space. The reciprocal space sampling was performed with a k-point grid of 4 × 4 × 4 points in the simulated cells, which contain 56 atoms. Self-consistent field cycles were converged to an energy difference of 2.7 × 10⁻⁶ eV.

Simulation and Fitting of the \(^{7}\)Li NMR Spectra. Random Solution Model of a Single Phase.

To use the Fermi contact bond pathway contributions calculated from DFT to simulate model NMR spectra, one needs to know the possible cationic environments around the lithium ion and the population distribution among these environments. The simplest approximation that can be made to obtain such distributions of environments is to consider that there is no cation ordering, and thus, the cations are randomly distributed in the sites available to them. This approach corresponds to the random solid solution model. In the regular spinel structure, Li centers have the following neighboring cations: (1) each Li in a Td site has 12 neighbor cations located on Oh sites, which are each bound via an oxygen bridge and considered to contribute to the overall Fermi contact shift of this lithium; and (2) each Li in an Oh site has 12 neighbor cations, 6 of which are in Td sites and 6 of which are in Oh sites, which are each bound via an oxygen bridge and considered to give (different) contributions to the overall Fermi contact shift of this lithium. To simulate the NMR spectrum, we thus need to know (i) how the Li ions are distributed between Td and Oh sites and (ii) what ions are present in each Li neighboring shell. Once we know these possible configurations, we can calculate the corresponding Fermi contact shifts and estimate the probability of these environments to simulate the NMR spectrum. In the random solution model, for each Li environment with a given number of Mn and Ti neighbors, the number of all possible configurations is calculated with the corresponding probability \(P\) modulated by the stoichiometric ratio of the ions in the structure. For each environment, a Gaussian distribution is then generated of the form \(G = p \exp[-(\delta - \delta_{\text{iso}})^2/(2\sigma^2)]\). In this formula, \(p\) is the probability associated with the environment considered, \(\delta\) is the range of resonance values for which the distribution is calculated, \(\delta_{\text{iso}}\) is the sum of all relevant bond pathway contributions to the shift involved in the particular environment, and \(\sigma\) is the Gaussian width. An approximate Gaussian peak width of 15 ppm was used to model the individual environments based on previous NMR studies on LiMn2O4.18 The simulated NMR spectrum is then obtained as the sum of the Gaussian plots corresponding to the various environments present in the system.

Revers Monaco Carlo Simulations of a Single Phase.

While in some cases, the random solution model provides a good agreement with the experimental data, in other cases, such as the LiTi1.5Mn0.5O4 material studied here, it does not, and there is a need to calculate the populations of lithium environments according to different conditions. Here, for this purpose, we use a simulation method inspired by reverse Monte Carlo approaches. The idea of a reverse Monte Carlo method is to build a large simulation box that is representative of the system under study and explore the effect of configurational changes. Starting from an initial configuration, i.e., a large number of ions with defined positions in space, we allow certain moves which are accepted or rejected depending on their agreement with chosen constraints.

In the present case, we built the large simulation box by replicating an initial spinel structure corresponding to LiTi1.5Mn0.5O4 in the P4\(_3\)32 space group. The initial structure contained 56 atoms corresponding to (i) 8 Li ions in Td sites (8c), (ii) 12 Ti ions and 4 Mn ions in Oh sites (12d and 4b, respectively), and (iii) 32 oxygen sites (8c and 24e). This simulation box was replicated 10 times in all 3 dimensions, leading to a large simulation box containing 8000 Li ions, 12 000 Ti ions, 4000 Mn ions, and 32 000 oxygen ions. We checked that this 10 × 10 × 10 system is large enough by simulating some of the NMR spectra with a larger box of 15 × 15 × 15 repeat units. The results from the two system sizes showed no significant differences, and so the size of the 10 × 10 × 10 cell was considered to be sufficient. Once the initial simulation box is built, the Monte Carlo method proceeds via the following steps: (1) swap two cations, (2) characterize the new Li environments, and (3) accept or reject the move according to a set of chosen rules. The swaps can be done between Li, Mn, and Ti belonging to octahedral sites (or to tetrahedral sites) or between cations belonging to different structural sites. If the simulations are done without constraints, all the swaps will be done randomly. If the simulations are done under constraints, the swaps which do not lead to Li environments conflicting with the set constraints will always be accepted, while the swaps leading to unwanted Li environments will be accepted with a small probability. The acceptance probability of unwanted moves is \(P_{\text{acc}} = \exp(-E_{\text{acc}}/T)\). Here, for all simulations, \(E_{\text{acc}}\) was taken to be 10 eV, i.e., the probability of having unwanted Li environments is very close to zero. In this work, the constraints are set based on the experimental Li NMR isotropic shifts. For example, if the spectrum of a particular composition does not show peaks at negative shifts, this is used as a constraint in the Monte Carlo simulation, which associates a small probability to the Li environments calculated to have negative shifts.

In addition to the swaps between the cations present in the structure, the Monte Carlo moves can include changes between different cation types. This is needed to reach some of the intermediate x values in the series. For example, on going from LiTi1.5Mn0.5O4 to LiTi1.5Mn0.5O4, a number of Ti ions need to be replaced by Mn ions and some Mn ions (only Mn oxidation state possible for LiTi1.5Mn0.5O4) will be converted to Mn5+ ions. These changes in cation types are also made with or without constraints. Once a satisfactory representation of the system has been reached, in terms of (i) Li distribution in Td and Oh sites and (ii) stoichiometry of the structure, the number of Li cations in each environment is simply counted, the corresponding shifts are calculated and, as in the random solution model representation, the simulated NMR spectrum is then obtained by summing the Gaussian plots corresponding to the various environments present in the system.

Model for Two Phase Systems.

The random solution model and Monte Carlo approaches described above were first used to simulate homogeneous (single-phase) systems. In the LiTiMn2O4 series, this single phase representation is able to depict only part of the series of materials. To investigate the possibility of having inhomogeneous
systems, we simulated independently two single-phase NMR spectra and summed them according to the fractions of the structure corresponding to each of the phases present in the system. In the Monte Carlo simulations, we built a single simulation box with two regions, each of the regions corresponding to a given phase.

■ RESULTS AND DISCUSSION

**Geometry Optimization and Energy Profile.** Figure 2 compares the formation energies of a number of structures in the LiTiiMn1.5xO4 series with formation energies below 0 eV, which are all obtained using the search strategy described in the previous section. The full set of simulated structures is shown in Figure S1 of the Supporting Information. The convex hull is indicated with a dashed line. Insets show the minimum-energy structure for each of the studied points of the series. The majority of the structures with energies plotted have Ti4+ ions on octahedral sites; those with Ti3+ on tetrahedral sites are indicated by blue circles corresponding to Oh Mn and outer magenta squares corresponding to Td Ti.

![Figure 2](image-url)

**Table 1. Summary of the Energetically Favorable Tetrahedral (Td) and Octahedral (Oh) Occupancies Obtained from the DFT Analysis of the Formation Energies throughout the LiTiiMn1.5xO4 Series**

| x in LiTiiMn1.5xO4 | 0.2 ≤ x ≤ 1.0 | x = 1.0 | 1.1 ≤ x ≤ 1.5 |
|---------------------|----------------|--------|--------------|
| Td sites            | Li<sup>+</sup> | Mn<sup>3+</sup> | Td sites | Oh sites | Li<sup>+</sup> | Mn<sup>3+</sup> | Mn<sup>3+</sup> | Mn<sup>2+</sup> | Mn<sup>2+</sup> |
| Oh sites            | Li<sup>+</sup> | Mn<sup>3+</sup> | Oh sites | Td sites | Li<sup>+</sup> | Mn<sup>3+</sup> | Mn<sup>3+</sup> | Mn<sup>2+</sup> | Mn<sup>2+</sup> |
| Li<sup>+</sup>      | Mn<sup>2+</sup> | Li<sup>+</sup> | Li<sup>+</sup> | Li<sup>+</sup> | Li<sup>+</sup> | Li<sup>+</sup> | Li<sup>+</sup> | Li<sup>+</sup> | Li<sup>+</sup> |
| Mn<sup>4+</sup>     | Mn<sup>4+</sup> | Mn<sup>3+</sup> | Mn<sup>3+</sup> | Mn<sup>3+</sup> | Mn<sup>3+</sup> | Mn<sup>3+</sup> | Mn<sup>3+</sup> | Mn<sup>3+</sup> | Mn<sup>3+</sup> |
| Ti<sup>4+</sup>     | Mn<sup>4+</sup> | Mn<sup>3+</sup> | Mn<sup>3+</sup> | Mn<sup>3+</sup> | Mn<sup>3+</sup> | Mn<sup>3+</sup> | Mn<sup>3+</sup> | Mn<sup>3+</sup> | Mn<sup>3+</sup> |

**Solid-State NMR.** Full one-dimensional 7Li double-adiaptic spin–echo<sup>31</sup> spectra of the LiTiiMn1.5xO4 powder samples (0.2 ≤ x ≤ 1.5) are given in Figure 3a. The double-adiabatic spin–echo sequence was chosen to obtain an efficient inversion of the whole spinning-sideband pattern, here of more than 400 kHz width.<sup>50</sup> The corresponding central regions of the spectra are shown in Figure 3b. The intensity ratio between the centerband and the sidebands did not change across the spectra, and for this reason we fit only the isotropic resonances. The variety of Li environments occurring in each phase leads to multiple distinct resonances and a broad isotropic region. The resonances, on average, range from around 500 to 30 ppm with the increase in Ti concentration. We also note that the spectrum is significantly broader for intermediate x values with the central regions covering a range of almost 600 ppm for 0.6 ≤ x ≤ 1.0. The distribution of discrete resonances giving rise to the broad spectra observed are due to Li ions in different local environments. These Li ions have different numbers of Mn<sup>2+</sup>, Mn<sup>3+</sup>, and Mn<sup>4+</sup> ions in their local coordination sphere, each contributing differently to the 7Li Fermi contact shift. The shifting of the resonances to lower frequency with the increasing Ti concentration is consistent with the decrease in...
the average Mn oxidation state and the decrease in the overall concentration of paramagnetic Mn ions. A more detailed understanding of the structural differences across the series is now presented based on the DFT analysis of the Fermi contact interaction.

### DFT Calculation of Magnetic and Hyperfine Parameters

As described previously (eq 3), the magnetic scaling of the hyperfine interaction was modeled via a mean field approach based on the exchange coupling interaction between Mn pairs, as shown in Figure 4. Mn\(^{3+}\) has a (t\(_{2g}\))^3 (e\(^g\))^1 electronic configuration, which makes it Jahn–Teller active. Consequently, different exchange couplings and Fermi contact interactions were identified, depending on whether the pathway involves the Jahn–Teller lengthened or shortened Mn–O bond. The calculated J\(_n\) values are presented in Table 2. The results agree well with the values reported by Lee et al. and Clément et al. for similar Mn oxides such as MgMn\(_2\)O\(_4\)\(^{33}\) and NaMnO\(_2\)\(^{32}\). Additionally, the accuracy of the calculated exchange integrals is tested for the LiTi\(_{0.4}\)Mn\(_{1.6}\)O\(_4\) case by comparing the magnetic scaling factors obtained with the mean field approach and using the experimental magnetic susceptibility. The computational and experimental results obtained are in good agreement, and the details of the comparison are presented in the Supporting Information. The magnitude of the exchange interactions is sensitive to the distance between the coupled ions as well as to the coupling mechanism between the involved orbitals. As an example, we compare the exchange interactions between Mn\(^{3+}\)–Mn\(^{3+}\) in octahedral sites. The J\(_1\) coupling (Figure 4, center) involves four Jahn–Teller shortened Mn–O bonds which allow direct overlap between the Mn t\(_{2g}\) orbitals, leading to a strong antiferromagnetic exchange interaction. The J\(_2\) coupling (Figure 4, center) involves two Jahn–Teller shortened and two Jahn–Teller elongated Mn–O bonds, the latter ones reducing the direct overlap between t\(_{2g}\) orbitals and hence the strength of the direct exchange interaction. The superexchange interaction between the orbitals along the Jahn–Teller axis (d\(^{x^2−y^2}\)−d\(_{z^2}\)) results in a combination of weak ferro- and antiferromagnetic interactions, resulting in a significantly smaller J\(_3\) coupling that is antiferromagnetic overall.

The possible Mn–O–Li bond pathways were identified for Li occupyingTd as well as Oh sites. All the Li environments and corresponding pathways are described in Figure 5 and are presented in Table 3. As rationalized by Carlier et al.\(^{51}\) the transfer of paramagnetic electron spin from the Mn t\(_{2g}\)/e\(^g\) orbitals to the s orbitals of the Li occur primarily via a superexchange-like mechanism. As presented in eq 1, the sign and magnitude of the Fermi contact shift are determined by a combination of factors. The extent of the transferred spin density as well as the strength of the magnetic interaction discussed previously strongly depend on the bond distances between the involved sites and on the orbitals involved in the interaction.\(^{51}\) The Mn–O–Li pathways in these systems

![Figure 3](image1)  
(a) \(^{7}\)Li NMR spectra of the LiTi\(_{0.2}\)Mn\(_{1.8}\)O\(_4\) series with the first-order sidebands enlarged in the top insets. (b) Expanded view of the isotropic resonances of the spectra.

![Figure 4](image2)  
Mn–Mn exchange coupling constants identified in the studied systems, i.e. LiTi\(_{1−x}\)Mn\(_x\)O\(_4\) for J\(_1\) and J\(_2\), LiTiMnO\(_4\) for J\(_3\) and J\(_4\), and LiTiMn\(_2\)O\(_4\) for J\(_5\). For each J\(_n\) the reported value corresponds to the average between the HYB20-HYB35 results.

| J\(_n\) | magnetic interaction | Mn–Mn angle (°) | HYB20 | HYB35 |
|-------|----------------------|-----------------|-------|-------|
| J\(_1\) | Mn\(^{2+}\)–Mn\(^{2+}\) JT short | 120.2 | −5 | −3 |
| J\(_2\) | Mn\(^{2+}\)–Mn\(^{2+}\) JT long | 120.1 | −1 | −1 |
| J\(_3\) | Mn\(^{2+}\)–Mn\(^{2+}\) JT short–JT long | 90.6 | 8 | −3 |
| J\(_4\) | Mn\(^{2+}\)–Mn\(^{2+}\) JT short–JT short | 97.2 | −41 | −32 |

For the couplings involving Mn\(^{3+}\) ions, the nature of Jahn–Teller lengthened or lengthened bond involved in the interaction is also specified. The results obtained with the HYB20 and HYB35 hybrid functionals are shown separately. Different J\(_n\) types are labeled as in Figure 4.
involve intermediate angles (neither exactly 90° nor exactly 180°); hence, the spin-density transfer deviates from a pure delocalization/polarization mechanism, and a complex combination of both processes is expected to occur. Nonetheless, we take the Li−O−Mn3+ pathways P1 and P2 (Figure 5, top) as examples to give an approximate rationalization of the mechanisms involved. The P1 pathway involves the Jahn−Teller shortened Mn−O bond with positive transfer of spin density from the dxy orbital via a delocalization mechanism. The P2 pathway involves the Jahn−Teller lengthened Mn−O bond, and a combination of positive delocalization/polarization transfer from the dxy orbital and a negative polarization transfer from the dz² orbital results in a weaker net Fermi contact interaction with the Li site.

Simulation and Fitting of the Experimental 7Li NMR Spectra. We now demonstrate how the bond pathway contributions calculated in Table 3 can be used to model the 7Li NMR spectra of the LiTi1−xMnxO4 series, allowing us to extract detailed local structural information. The shift values calculated with the HYB20 and HYB35 functionals give the upper and lower bounds; however, in the following analysis, we use a pragmatic approach in which the HYB20 and HYB35 results are averaged to give a single value for each pathway P, as shown in Table 3. For all the systems containing Mn3+, we model the Jahn−Teller distortion as a dynamic process in which the time scale of the changes in local Mn−O bond lengths is much faster than the typical NMR time scale. As a consequence, we assume that the shifts corresponding to Mn3+−O−Li are well-represented by a weighted average with 2/3 of Jahn−Teller-short and 1/3 of Jahn−Teller-long pathway contributions.

For all the systems containing exclusively Mn3+ and Mn4+ ions, i.e. the 0.2 ≤ x ≤ 0.8 stoichiometries, we make an additional assumption. In this case, we consider that the time scale of electronic conduction is fast compared to the NMR time scale. This means that we can consider only one shift corresponding to an average oxidation state of the Mn ions. The weighted average depends on the stoichiometry of the system, as the average oxidation state is a function of the Ti content of the material. For example, for LiTi0.2Mn1.8O4, the average Mn oxidation state is 3.444, while it is 3.375 for LiTi0.6Mn1.4O4. As a result, the net shift contributions are 41 ppm for a Mn3.44+ in LiTi0.2Mn1.8O4, 39 ppm for a Mn3.38+ in LiTi0.4Mn1.6O4, 37 ppm for a Mn3.29+ in LiTi0.6Mn1.4O4, and 33 ppm for a Mn3.17+ in LiTi0.8Mn1.2O4. This assumption, as well as the accuracy of the calculated bond pathway shift contributions is tested with respect to the 7Li NMR shift of LiMn2O4. This material has been extensively studied with NMR: as discussed in detail by Lee et al.,18 the NMR spectrum of LiMn2O4 with Li in the tetrahedral 8a position is dominated by one major resonance with an isotropic shift of 512−520 ppm, the exact value varying between samples and likely the temperature of the measurement. In this stoichiometry, Mn is present in an average oxidation state of 3.5+. Combining the shift contributions that we obtained with DFT, summarized in Figure 5.

![Figure 5. 7Li bond pathway contributions to the Fermi contact shift for a lithium center (in green) in a tetrahedral site (top) or in an octahedral site (bottom), each coordinated by 12 TM sites (in purple) via oxygen (in red) bonds. Manganese is shown in yellow, blue, and gray for Mn2+, Mn3+, and Mn4+, respectively. For each bond pathway contribution P, the reported value corresponds to the average between the HYB20-HYB35 results.](image)

Table 3. Comparison of the Calculated Mn−O−Li Pathway Contributions to the 7Li Fermi Contact Shift Obtained with Either the HYB20 or HYB35 Functional

| Li environment | pathway | Mn neighbor | Mn−Li distance (Å) | Mn−O−Li angle (°) | shift H20; H35 (ppm) | average shift (ppm) |
|----------------|---------|-------------|--------------------|-------------------|----------------------|---------------------|
| Li Td          | P1      | Mn3+ Oh JT short | 3.5                | 120.2             | 34; 39               | 37                  |
|                | P2      | Mn3+ Oh JT long  | 3.6                | 114.0             | 10; 16               | 13                  |
|                | P3      | Mn2+ Oh        | 3.5                | 115.2             | 24; 32               | 28                  |
|                | P4      | Mn4+          | 3.5                | 116.2             | 50; 64               | 57                  |
| Li Oh          | P1      | Mn3+ Td        | 3.5                | 114.0             | 15; 18               | 17                  |
|                | P2      | Mn3+ Oh        | 3.0                | 92.3              | −54; −73             | −64                 |
|                | P3      | Mn4+ Oh JT long | 3.6                | 91.6              | 150; 98              | 124                 |
|                | P4      | Mn4+ Oh        | 3.5                | 92.0              | 213; 151             | 181                 |

The table rows on the top (P1 to P4) show the possible neighboring TM sites transferring unpaired-electron spin density to a Li center in a tetrahedral site, while the table rows on the bottom (P1 to P4) show the possible sites transferring unpaired-electron spin density to a Li center in an octahedral site. Pathways are labelled as in Figure 5.
Moreover, the relative intensities of the distribution of Ti$^{4+}$ and Mn$^{3.44+}$ among the octahedral sites. The accurately reproduced by the model that considers a random neighbors. The weak peak at 595 ppm is also predicted by DFT with the model corresponding to each resonance DFT-calculated pathway contributions. The Li environment associated total Fermi contact shift obtained as a sum of the resonances corresponding to each Li environment with the 6b. The spectrum is obtained as a Gaussian distribution of shown in Figure 6a with the individual peaks shown in Figure 6b. The spectrum is obtained as a Gaussian distribution of resonances corresponding to each Li environment with the associated total Fermi contact shift obtained as a sum of the DFT-calculated pathway contributions. The Li environment corresponding to each resonance differs from the others by the number of Ti centers among the 12 neighboring sites.

The experimental $^7$Li NMR spectrum of LiTi$_{0.2}$Mn$_{1.8}$O$_4$ was then fitted, as shown in Figure 6a. A good fit is obtained by using five more intense peaks of Voigt line shape and two very weak peaks. The shift contributions predicted with DFT match very well with the values obtained from the experimental fit with a maximum discrepancy of 16 ppm. The 5 main peaks extracted from the fit are assigned to Li sites with 12 Mn neighbors (fit: 512 ppm, DFT: 496 ppm), 11 Mn and 1 Ti neighbors (fit: 464 ppm, DFT: 454 ppm), 10 Mn and 2 Ti neighbors (fit: 417 ppm, DFT: 413 ppm), 9 Mn and 3 Ti neighbors (fit: 370 ppm, DFT: 372 ppm), and 8 Mn and 4 Ti (fit: 324 ppm, DFT: 331 ppm), as shown in Figure 6a. Moreover, the relative intensities of the different peaks are accurately reproduced by the model that considers a random distribution of Ti$^{4+}$ and Mn$^{3.44+}$ among the octahedral sites. The weak peak at 595 ppm is also predicted by DFT with the model that does not consider a dynamic exchange between Mn$^{3+}$ and Mn$^{4+}$. In particular, the shift of the Li environment coordinated with 3 Mn$^{3+}$ and 9 Mn$^{4+}$ is calculated to be 599 ppm, in good agreement with the experimental shift of 595 ppm.

Figure S2 in the Supporting Information shows the results of the model that does not consider a dynamic exchange between Mn$^{3+}$ and Mn$^{4+}$. The line shape of the spectrum simulated in this way is not in as good agreement with the experimental NMR spectrum, confirming that the fast Mn$^{3+/4+}$ hopping rate in the experimental NMR conditions is a good assumption for these systems.

$0.4 \leq x < 1.0$ Stoichiometries. Following the successful description of the cation ordering for LiTi$_{0.2}$Mn$_{1.8}$O$_4$ with the random distribution model, we apply the same approach for the $0.4 \leq x < 1.0$ stoichiometries. As shown in Figure S3 of the Supporting Information, the deconvolution of the isotropic region for LiTi$_{0.2}$Mn$_{1.8}$O$_4$ deviates significantly from the spectrum simulated for the random distribution model. The disagreement between the experimental NMR spectra and the simulations based on the random distribution model persists for all the $0.4 \leq x < 1.0$ cases, as shown in Figure S4 of the Supporting Information.

By comparing the NMR fit of the isotropic region for LiTi$_{0.2}$Mn$_{1.8}$O$_4$ (Figure 6a) and that of LiTi$_{0.4}$Mn$_{1.6}$O$_4$ (Figure S3), we notice that (i) the major contributing peaks of the $x = 0.2$ spectrum have the same shifts as 5 of the major peaks in the $x = 0.4$ case and (ii) the spectrum of the $x = 0.4$ case shows an additional broad feature that extends between 300 and 100 ppm, which is absent in the spectrum of $x = 0.2$. In LiTi$_{0.2}$Mn$_{1.8}$O$_4$, Mn has a net charge of 3.44+, while in LiTi$_{0.4}$Mn$_{1.6}$O$_4$, Mn has a net charge of 3.375+, each with different Fermi contact shift contributions to the neighboring Li center (41 ppm for Mn$^{3.44+}$ and 39 ppm for Mn$^{3.375+}$). The fact that the fits of the spectra for the $x = 0.2$ and for the $x = 0.4$ cases give the major peaks at exactly the same shifts indicate that in the $x = 0.4$ cases this correspond to Mn$^{4+}$-rich Li environments. The spectrum of the $x = 0.4$ case simulated for the random Mn$^{3.375+}$-Ti distribution does not show shifts lower than 204 ppm, in disagreement with the experimental spectrum. This suggests the presence of Mn$^{3+}$-rich Li environments in the structure. The $^7$Li isotropic region for LiTi$_{0.2}$Mn$_{1.8}$O$_4$ is hence modeled as a 1:1 combination (i.e., an average) of the LiTi$_{0.2}$Mn$_{1.8}$O$_4$ and LiTi$_{0.4}$Mn$_{1.6}$O$_4$ experimental spectra. The resulting peaks, shown in Figure 7, reproduce the experimental spectrum of the $x = 0.4$ case very well, indicating a coexistence of Mn$^{4+}$-rich and Mn$^{3+}$-rich domains.

The spectra for the $x = 0.6$ and 0.8 show a gradual shift of resonances toward lower frequency with the increasing Ti
concentration, indicative of a continuous solid solution behavior.\textsuperscript{16} LiTiMnO\textsubscript{4}. As described in Figure 2 and in Table 1, for the $x=1$ case, our calculations predicted that the configuration with mixed Li$^{+}$, Mn$^{2+}$ tetrahedral and Li$^{+}$, Mn$^{3+}$/4+ octahedral occupancies is more favorable than the normal spinel (Li[Mn$^{3+}$Ti$^{2+}$]O$_{4}$). Studies based on X-ray diffraction reported \textsuperscript{20}−30% Li occupancy of the Oh site (or, equivalently, 20−30% Mn$^{2+}$ on the Td site).\textsuperscript{15,16} In an attempt to model the spectrum for LiTiMnO$\textsubscript{4}$, we hence consider a random cation distribution for the normal spinel lattice (Li[Mn$^{3+}$Ti$^{2+}$]O$_{4}$) as well as for the partially inverse lattice with 30% site inversion (Li$_{0.7}$Mn$_{0.3}$\textsuperscript{2+} [Li$_{0.3}$Mn$_{0.4}$\textsuperscript{3+Mn$_{0.3}$\textsuperscript{4+Ti}]O$_{4}$). The results are shown in Figure 8.

The spectrum simulated for the partially inverse case (Figure 8b) shows shifts over the entire 0−700 ppm region of the experimental spectrum, while the simulation for the normal spinel (Figure 8a) shows shifts only between 20−300 ppm. This confirms the presence of both Li(Td) and Li(Oh) environments in the structure, as predicted by our calculations (Table 1). However, the line shape of the experimental spectrum is not well reproduced by the simulation for the disordered Li$_{0.7}$Mn$_{0.3}$\textsuperscript{2+} [Li$_{0.3}$Mn$_{0.4}$\textsuperscript{3+Mn$_{0.3}$\textsuperscript{4+Ti}]O$_{4}$ lattice, particularly between 0−100 and 350−450 ppm. This indicates that the cations are not distributed randomly in the structure, and cation ordering determines the preferential presence of certain environments over others. Due to the configurational complexity of the system, which contains Li/Mn$^{2+}$/3+/4+/Ti ions and mixed occupancy of the Td and Oh sites, further work would be needed to systematically analyze the configurational energies of different orderings\textsuperscript{52} and possibly account for the electroneutrality principle.

LiTi$_{1.5}$Mn$_{0.5}$O$_{4}$. We now turn to the interpretation of the NMR spectra for the Ti-rich part of the series, starting with the end member LiTi$_{1.5}$Mn$_{0.5}$O$_{4}$. In this system, we expect Li$^{+}$, Mn$^{2+}$, and Ti$^{4+}$ cations to be present. The formation energies calculated with DFT shown in Figure 2 indicate that it is energetically favorable for Mn$^{2+}$ ions to be on tetrahedral sites, leading to (at least) a fraction of the Li ions on the octahedral sites, also suggested by previous X-ray studies.\textsuperscript{16} This fraction is referred to as the inverted fraction of Li, $y$, in the notation Li$_{1−y}$Mn$_{y}$[Li$_{y}$Ti$_{1.5}$Mn$_{0.5}$]$^{−y}$O$_{4}$. The first model we test is a random distribution of Mn$^{2+}$/Li$^{+}$ ions on tetrahedral sites and Li$^{+}$/Mn$^{2+}$/Ti$^{4+}$ on octahedral sites. The simulated NMR spectra are shown in Figure S5 of the Supporting Information for various inverted fractions of Li from $y = 0.0$ (i.e., Li[Ti$_{1.5}$Mn$_{0.5}$]$^{-}O_{4}$) to $y = 0.5$ (i.e., Li$_{0.5}$Mn$_{0.5}$[Li$_{0.5}$Ti$_{1.5}$]$^{−}O_{4}$). When the inverted fraction is $y = 0.5$, all Mn$^{2+}$ are on tetrahedral sites; half of the Li ions are on octahedral sites, and half of the Li ions are on tetrahedral sites. None of the spectra show good agreement with the experiment. The simulated spectra show two main features in strong disagreement with the experimental data, i.e. resonances at 0 ppm and some at negative frequencies, which are clearly not present in the experimental NMR spectrum. To use this information, we thus turn to another strategy and follow an approach similar to reverse Monte Carlo, where constraints are imposed. We use as a starting point a spinel structure with a $P4_{3}32$ symmetry, as this was suggested by X-ray studies on this material.\textsuperscript{16} In our starting $P4_{3}32$ structure, the lattice is characterized by a full Li occupancy on the tetrahedral sites and a full Ti/Mn occupancy of the octahedral sites (i.e., a regular spinel structure). This ordering corresponds to the

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure7.png}
\caption{Comparison of the experimental isotropic region of the $^7$Li NMR spectrum of LiTi$_{0.2}$Mn$_{1.8}$O$_{4}$ (in red), LiTi$_{0.4}$Mn$_{1.6}$O$_{4}$ (in green), and LiTi$_{0.6}$Mn$_{1.4}$O$_{4}$ (in black), and the calculated LiTi$_{0.4}$Mn$_{1.6}$O$_{4}$ (in dashed green) isotropic peak. This is obtained by taking the average of the peaks of $x = 0.2$ and 0.6.}
\end{figure}

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure8.png}
\caption{Comparison of the experimental isotropic region of the $^7$Li NMR spectrum of LiTiMnO$_{4}$ (solid black line) with the simulated spectrum of the normal Li[TiMn$^{3+}$]$^{-}$O$_{4}$ (dashed red line, a), and the simulated spectrum of the partially inverse Li$_{0.7}$Mn$_{0.3}$\textsuperscript{2+} [Li$_{0.3}$Mn$_{0.4}$\textsuperscript{3+Mn$_{0.3}$\textsuperscript{4+Ti}]O$_{4}$ (dashed red line, b). Also shown are the peaks corresponding to Li(Td) environments (dashed blue lines) and to Li(Oh) environments (dashed gray lines).}
\end{figure}
presence of only one type of Li environment with 9 Ti\textsuperscript{4+} and 3 Mn\textsuperscript{3+} neighbors. The calculated shift is 3 \times 28 ppm = 85 ppm, in clear disagreement with the experimental NMR (Figure 9a).

Starting from the fully regular structure, the Monte Carlo simulation then allowed for some fraction of Li to move onto the octahedral environment with the consequent swap of Mn (and Ti) onto the tetrahedral sublattice. After each swap, the Li coordination environments are checked, and the corresponding shifts are calculated. If the swap leads to a “wrong” shift (a shift \leq 0 ppm), it will be accepted but only with a very low probability.

The results of the reverse Monte Carlo approach are shown in Figure 9a. The best agreement between simulation and experiment is obtained for the y = 0.4 case, shown more in detail in Figure 9b, corresponding to the Li\textsubscript{0.6}Ti\textsubscript{0.1}Mn\textsubscript{0.3}O\textsubscript{4} lattice of P4\textsubscript{3}32 symmetry with the repeated unit shown in the inset of Figure 9b. The Li environments present in the lattice are also shown with the associated NMR peaks. The good agreement between the model and the experimental spectrum allows us to conclude that the spinel network of the LiTi\textsubscript{1.1}Mn\textsubscript{0.5}O\textsubscript{4} system, of P4\textsubscript{3}32 symmetry as previously reported,\textsuperscript{16} contains mixed cation occupancy of Li, Mn\textsuperscript{2+}, and Ti in both tetrahedral and octahedral environments. The presented analysis also allows us to derive a specific cation ordering within P4\textsubscript{3}32 plane. (Li\textsubscript{0.6}Ti\textsubscript{0.1}Mn\textsubscript{0.3})\textsubscript{16}O\textsubscript{4} and (Li\textsubscript{0.3}Ti\textsubscript{1.4}Mn\textsubscript{0.2})\textsubscript{48}O\textsubscript{4}.

1.1 \leq x \leq 1.4 Stoichiometries. The reverse Monte Carlo approach was implemented further to analyze the NMR spectra of the intermediate 1.1 \leq x \leq 1.4 systems. We first look at the LiTi\textsubscript{1.1}Mn\textsubscript{0.9}O\textsubscript{4} material using exactly the same approach as for LiTi\textsubscript{1.1}Mn\textsubscript{0.5}O\textsubscript{4} but now having a mix of Mn\textsuperscript{3+} and Mn\textsuperscript{2+} ions.

As highlighted previously from the DFT results, the presence of Mn\textsuperscript{3+} on tetrahedral sites is unfavorable. The NMR spectra simulated for a homogeneous Li0.6Ti0.1Mn0.3[Li0.4Ti1.4Mn0.2]O4 lattice of \textit{Fd}3\textmit{m} stoichiometry as previously reported,\textsuperscript{16} contains mixed cation disorder found at intermediate 0.2 \leq x \leq 1 values of the Mn\textsuperscript{3+} phase compared to the \textit{Fd}3\textmit{m} symmetry. As NMR probes structural short-range ordering, it does not allow us to distinguish the sizes of the \textit{Fd}3\textmit{m} and the P4\textsubscript{3}32 phases. Because previous diffraction studies,\textsuperscript{16} which are sensitive to long-range ordering, reported a single P4\textsubscript{3}32 phase behavior for 1.2 \leq x \leq 1.4, this may suggest that the \textit{Fd}3\textmit{m}–P4\textsubscript{3}32 phase segregation is on the local scale, potentially forming small domains.

The combination of first-principles shift calculations, random solution/Monte Carlo model, and experimental NMR enabled us to acquire a detailed understanding of the complex trend of cation ordering in the mixed LiTi\textsubscript{1.1}Mn\textsubscript{0.5}O\textsubscript{4} series. This is of particular interest in regards to the application of this material as a cathode in rechargeable Li-ion batteries. The high degree of cation disorder found at intermediate 0.2 \leq x \leq 1 values of the
series may hinder a cooperative Jahn–Teller distortion in the bulk and facilitate the mechanical stability during electrolyte cycling. On the other hand, the observed increasing ratio of Li(Oh)/Mn2+(Td) mixing with increasing x may hinder the extraction of Li+ from the structure, effectively resulting in a lower capacity.

**CONCLUSIONS**

A detailed solid-state 7Li NMR and first-principles DFT study of the cation ordering and the structural changes in the LiTi1−xMn2+xO4 series (0.2 ≤ x ≤ 1.5) was presented. 7Li MAS NMR spectra were obtained for the LiTi1−xMn2+xO4 series using state of the art spectroscopic methods for paramagnetic solids. The methodology used to analyze the NMR results involved the ab initio calculation of the magnetic and hyperfine parameters, obtaining a breakdown of the possible contributions to the 7Li NMR shift. These were combined into random distribution and reverse Monte Carlo models to simulate the 7Li NMR spectra of the LiTi1−xMn2+xO4 series. For x = 0.2, a random distribution of octahedral Mn3+/4+/Ti4+ cations in the Fd3m structure was determined, evolving into an inhomogeneous lattice of Mn3+−rich/Mn4+−rich phases for x = 0.4 and a single-phase solid solution for x = 0.6 and 0.8. The x = 1.0 case showed partially inverse ordering of Mn3+/4+/Ti4+−Li (Oh) and Mn2+/−Li(Td) sites. In the 1.1 ≤ x ≤ 1.5 structures, the results showed the preferential formation of coexisting disordered Mn3+−rich (Fd3m) and ordered Mn2+−rich (partially inverse P4321) phases. Additionally, for LiTi1−xMn2−xO4 a specific cation ordering within the partially inverse spinel framework of P4321 symmetry was determined, i.e. (Li0.3TixMn2−xO4).[Li0.3TixMn2−xO4]. The ability of the DFT results to reproduce the experimental 7Li NMR data is promising. The presented methodology in general and the DFT-calculated 7Li NMR shifts in particular pave the way to a detailed rationalization of the solid-state NMR spectra of other paramagnetic solids. The combination of the calculated NMR shifts with the random distribution and reverse Monte Carlo methods represents a robust approach which can be extended to include additional energetic/configurational constraints to analyze other complex systems of interest to the battery field such as LiZnMn2−xO4, LiNiMn2−xO4, and the Li-excess Li1+Mn2−xO4 materials.

**ASSOCIATED CONTENT**

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.chemmater.7b04314.

Additional computational details, synthesis procedure, complete convex hull, additional lattice simulations, and details and results of magnetic SQUID measurements (PDF)

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**Notes**

The authors declare no competing financial interest.

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SUPPORTING INFORMATION

Structural characterization of the Li-ion battery cathode materials \( \text{LiTi}_x\text{Mn}_{2-x}\text{O}_4 \) (0.2 \( \leq x \leq 1.5 \)):
A combined experimental \(^{7}\text{Li} \) NMR and first-principles study

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Synthesis of LiTi$_x$Mn$_{2-x}$O$_4$ (0.2 $\leq x \leq$ 1.5)

Stoichiometric ratios of Li$_2$CO$_3$ (dried at 120°C, Merck, 99%), MnCO$_3$ (Sigma-Aldrich, 99%) and TiO$_2$ (Aithaca, 99%) were ground in a small amount of acetone until dry, then transferred into alumina crucibles and fired at 500°C for 12 hours. The calcined samples were re-ground with acetone until dry and pressed into pellets using a uniaxial pellet press at 8 tons of pressure. Samples were further sintered in air at 900°C for 24 hours, then quenched in liquid nitrogen, with the exception of LiTi$_{0.2}$Mn$_{1.8}$O$_4$, LiTi$_{1.4}$Mn$_{0.6}$O$_4$ and LiTi$_{1.5}$Mn$_{0.5}$O$_4$ which were slow-cooled in air after sintering, the latter two samples being further heated in argon for 3 hours.
Previous XRD refinement results of the LiTi$_x$Mn$_{2-x}$O$_4$ series

Table S1: Crystal data and cation compositions of the LiTi$_x$Mn$_{2-x}$O$_4$ series ($x = 0.2, 0.4, 0.6, 0.8, 1.0, 1.2, 1.3, 1.5$), summarized from Ref. 1.

| $x$ | Space Group | $a$ - Å | Partial Occupancies |
|-----|-------------|---------|---------------------|
| 0.2 | Fd$ar{3}$m | 8.2643  | 8a: Li$^+$ (0.98), Mn$^{2+}$ (0.02)  
      |            |         | 16d: Ti$^{4+}$ (0.10), Mn$^{3+/4+}$ (0.89), Li$^+$ (0.01) |
| 0.4 | Fd$ar{3}$m | 8.3049  | 8a: Li$^+$ (0.91), Mn$^{2+}$ (0.09)  
      |            |         | 16d: Ti$^{4+}$ (0.20), Mn$^{3+/4+}$ (0.76), Li$^+$ (0.04) |
| 0.6 | Fd$ar{3}$m | 8.3313  | 8a: Li$^+$ (0.84), Mn$^{2+}$ (0.16)  
      |            |         | 16d: Ti$^{4+}$ (0.30), Mn$^{3+/4+}$ (0.62), Li$^+$ (0.08) |
| 0.8 | Fd$ar{3}$m | 8.3586  | 8a: Li$^+$ (0.78), Mn$^{2+}$ (0.22)  
      |            |         | 16d: Ti$^{4+}$ (0.40), Mn$^{3+/4+}$ (0.49), Li$^+$ (0.11) |
| 1.0 | Fd$ar{3}$m | 8.3833  | 8a: Li$^+$ (0.70), Mn$^{2+}$ (0.30)  
      |            |         | 16d: Ti$^{4+}$ (0.50), Mn$^{3+/4+}$ (0.35), Li$^+$ (0.15) |
| 1.2 | P4$_3$32   | 8.4062  | 8c: Li$^+$ (0.61), Mn$^{2+}$ (0.39)  
      |            |         | 12d: Ti$^{4+}$ (0.80), Mn$^{3+/4+}$ (0.19), Li$^+$ (0.01)  
      |            |         | 4b: Li$^+$ (0.75), Mn$^{3+/4+}$ (0.25) |
| 1.3 | P4$_3$32   | 8.4186  | 8c: Li$^+$ (0.57), Mn$^{2+}$ (0.43)  
      |            |         | 12d: Ti$^{4+}$ (0.87), Mn$^{3+/4+}$ (0.10), Li$^+$ (0.03)  
      |            |         | 4b: Li$^+$ (0.77), Mn$^{3+/4+}$ (0.23) |
| 1.5 | P4$_3$32   | 8.4369  | 8c: Li$^+$ (0.50), Mn$^{2+}$ (0.50)  
      |            |         | 12d: Ti$^{4+}$ (1.0)  
      |            |         | 4b: Li$^+$ (0.99), Mn$^{3+/4+}$ (0.01) |
Description of the Basis Sets

All-electron atom-centered basis sets comprising fixed contractions of Gaussian primitive functions are employed throughout for the calculations done with CRYSTAL. Two levels of basis sets are used: the first and smaller set used for geometry optimizations is of the form $(7s\ 2p\ 1d)/[1s\ 2sp\ 1d]$ for Li; $(10s\ 4p\ 1d)/[1s\ 2sp\ 1d]$ for O; and $(20s\ 12p\ 5d)/[1s\ 4sp\ 2d]$ for Mn and Ti, where the values in parentheses indicate the number of primitives within each shell and the values in square brackets the contraction scheme.\textsuperscript{2} In the more extended provision used for the calculation of hyperfine $A^{FC}$ and $A^{dip}$ parameters, modified IGLO-III sets are adopted for O, taking the form $(10s\ 6p\ 2d)/[6s\ 5p\ 2d]$ for O.\textsuperscript{3} A flexible and extended TZDP-derived basis of the form $(9s\ 2p)/[5s\ 2p]$ is used for Li, and Ahlrichs DZP-derived sets of the form $(13s\ 9p\ 5d)/[7s\ 5p\ 3d]$ are applied for Mn and Ti.\textsuperscript{3} These sets are consistent with those used in a recent previous calculation of hyperfine parameters in a series of Mn-oxides.\textsuperscript{4,5}
Convex Hull

Figure S1: Formation energy per LiTi$_x$Mn$_{2-x}$O$_4$ formula unit vs fractional Ti concentration in the LiTi$_x$Mn$_{2-x}$O$_4$ series. The convex hull is indicated with a dashed line. Insets show the minimum-energy structure for each of the studied points of the series. With the exception of LiTi$_2$O$_4$ configurations, all other structures with energy plotted in the Figure have Ti$^{4+}$ ions on octahedral site, while the presence of Ti$^{4+}$ on tetrahedral sites is indicated by the outer magenta square.
Li NMR analysis

Figure S2: Comparison between the experimental (solid black line) and the simulated $^7$Li spectrum of LiTi$_{0.2}$Mn$_{1.8}$O$_4$ based on the random solution model, assuming a dynamic exchange (dotted red line) and no exchange (dotted blue line) between Mn$^{3+}$ and Mn$^{4+}$. 
Figure S3: Results of the fitting of the $^7$Li NMR spectrum for the LiTi$_{0.4}$Mn$_{1.6}$O$_4$, and comparison with the random model predicted with DFT.
Figure S4: Comparison of the experimental isotropic region (in solid line) of the $^7$Li NMR spectrum of LiTi$_x$Mn$_{2-x}$O$_4$, and the simulated region assuming a random distribution of Ti$^{4+}$ and Mn$^{3+/4+}$ in a single-phase model (dashed line). The red, green, black, magenta and blue lines are for $x = 0.2$, 0.4, 0.6, 0.8, 1, respectively.
Figure S5: Isotropic region of the experimental $^7$Li NMR spectrum of LiTi$_{1.5}$Mn$_{0.5}$O$_4$ (dotted black line), and the NMR results of the Monte Carlo simulation of Li$_{1-y}$Mn$_y$[Li$_y$Ti$_{1.5}$Mn$_{0.5-y}$]O$_4$. Red, green blue, magenta, yellow and cyan lines for $y$=0, 0.1, 0.2, 0.3 and 0.4, respectively.
Figure S6: Isotropic region of the experimental $^7$Li NMR spectrum of LiTi$_{1.4}$Mn$_{0.6}$O$_4$ (dotted black line), and the NMR results of the constrained Monte Carlo simulation of Li$_{1-y}$Mn$_y$[Li$_y$Ti$_{1.4}$Mn$_{0.6-y}$]O$_4$. Red, green, blue and magenta lines for $y=0$, 0.1, 0.2, and 0.3, respectively, and yellow line for Li$_{0.6}$Ti$_{0.1}$Mn$_{0.3}$[Li$_{0.4}$Ti$_{1.3}$Mn$_{0.3}$]O$_4$

**Magnetic scaling factor for LiTi$_{0.4}$Mn$_{1.6}$O$_4$**

The magnetic Hamiltonian of the assumed Ising-type system, $H_0$, takes the form of

\[ H_0 = E_0 - \sum_n \sum_{i,j} J_n S_i S_j \]  

(S1)

with $E_0$ being the energy of the system excluding all the magnetic interactions, $n$ the order of the interaction over the neighbouring shells, $S$ the spin value of the $(i,j)$ interacting sites with the respective exchange coupling constant, $J$, and where all the $2S+1$ projections of the spin along $z$ are included. In this work, $J$ is determined by a multivariate linear regression of the energies of systems having different magnetic configurations of the coupled spins, calculated with DFT. The total exchange interaction at a site $i$, given by all the couplings
with the neighbouring spins, is expressed as a mean field, which is felt by spin $i$, as well as by the neighbouring spins. The time-averaged spin of a site $i$, $\langle S_{z,i} \rangle$, is obtained by calculating the Brillouin function at a particular temperature and external magnetic field, and the mean field equations are solved self consistently for all the spins in the cell. From the calculated $\langle S_{z,i} \rangle$, one can evaluate the magnetic scaling factor either for the total unit, or, like in this work, for a specific site, $i$, such as $\Phi_i = \frac{\langle S_{z,i} \rangle}{S_i}$.

The accuracy of the calculated $J_n$ values is validated for a test case, LiTi$_{0.4}$Mn$_{1.6}$O$_4$. Magnetization measurements were performed for the LiTi$_{0.4}$Mn$_{1.6}$O$_4$ powder sample with Quantum Design Material Property Measurement System (MPMS). The magnetic susceptibility of the zero field-cooled sample was measured over the temperature range 2 – 350K, under the external field of 100 Oe.

The LiTi$_{0.4}$Mn$_{1.6}$O$_4$ molar magnetic susceptibility measured experimentally over the 2 – 350K temperature range is shown in Fig. S7.

![Figure S7: Experimental molar magnetic susceptibility vs. temperature curve for LiTi$_{0.4}$Mn$_{1.6}$O$_4$.](image-url)
As derived by Kim et al., the bulk value for the magnetic scaling factor can be calculated from the experimental molar magnetic susceptibility (using the equivalent expression presented by Clément et al.):

\[
\Phi = \frac{B_0 \chi_m}{g_e \mu_B S N_A}
\]  

(S2)

where \( B_0 \) is the external magnetic field strength, \( \chi_m \) is the experimental molar magnetic susceptibility, \( g_e \) is the free electron g-value, \( \mu_B \) is the Bohr magneton, \( S \) is the formal spin of the transition metal species and \( N_A \) is Avogadro’s number.

In the case of LiTi\(_{0.4}\)Mn\(_{1.6}\)O\(_4\) presented here, a bulk molar susceptibility of \( 7.69 \times 10^{-3} \) emu.mol\(^{-1}\) is obtained at the temperature of 320 K. Taking \( B_0 = 4.72 \) T as the NMR external magnetic field, the net oxidation state of \( \text{Mn}^{3.375+} \), hence \( S = 1.8125 \), and using eq. S2 with the experimental value of \( \chi_m \), a bulk magnetic scaling factor \( \Phi_{\text{expt}} = 0.024 \) is obtained. This result is compared with the value of the bulk magnetic scaling factor calculated with Mean Field approach described in Section 3.2.1 of the main article, using the computed exchange coupling constants \( J_3 - J_4 - J_5 \) summarized in Table 2. A lattice of LiTi\(_{0.4}\)Mn\(_{1.6}\)O\(_4\) composition is simulated, containing 51 Mn sites, and a bulk magnetic scaling factor \( \Phi_{\text{MeanField}} = 0.018 \) is obtained at the temperature of 320 K. The values obtained using the experimental \( \chi_m \) and the Mean Field approach are in good agreement, indicating that the calculated exchange constants are reasonably accurate.

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