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DFT-assisted solid state NMR characterization of defects in Li_2MnO_3

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Abstract

The complete description of defective structures and their impact on materials behavior is a great challenge due to difficulties associated with their reliable characterization in the nanoscale. In this paper density functional theory (DFT) calculations are used to elucidate the solid state nuclear magnetic resonance (NMR) spectra of Li_2MnO_3 which, combined with X-ray diffraction (XRD), provide a full description of disorder in this compound. While XRD allows accurate quantification of planar defects, the use of solid state NMR reveals limited vacancy concentrations that were undetected by XRD as NMR is highly sensitive to the atomic local environments. The combination of these methods is here proven to be highly effective in overcoming the challenges of describing in great detail limited concentrations of disorder in transition metal oxides, providing information about structural variables that are essential to their application.

Introduction

In many functional materials defects form complex structures whose reliable description is of extreme relevance to understand their effect on material's properties. Correlating defects and defect interactions with function remains however a great challenge and requires a combined approach. Solid state nuclear magnetic resonance (NMR) is a very useful technique for the evaluation and quantification of the structural features of a material at a local level and offers a very interesting perspective for the full structural description of a material in combination with the global picture provided by X-ray diffraction (XRD).¹⁻⁵ In particular, solid state NMR of paramagnetic cathode materials is very sensitive to local discontinuities as the magnetic interactions governing the NMR spectra of these materials are strongly affected by even very minor changes in the bond distances and angles linking the atoms.⁴⁻⁷

The accurate description and quantification of defects in polycrystalline materials such as transition metal oxides provides very valuable information, as proper understanding of the underlying thermodynamics and kinetics of functional materials unavoidably requires the framework of both structure and microstructure. This is particularly the case of Li-rich cathode materials ($x\text{Li}_2\text{MnO}_3 \cdot (1-x)\text{LiMO}_2$ or $\text{Li}_{1+x}\text{M}_{1-x}\text{O}_2$, where M is typically Mn, Ni, Co), which represent a transformational approach for creating advanced energy materials as they combine the beneficial effects of standard cationic redox activity with new reversible anionic redox processes, resulting in remarkable capacities.⁸⁻¹¹ However, these materials are known to suffer from fast voltage and capacity fading as a consequence of a major structural reorganization occurring upon cycling that is still the object of intense research.¹²⁻¹⁹ Significant efforts have been taken in recent years to understand and overcome these issues to foster their commercial implementation (including synthetic methods,²⁰⁻²³ chemical modifications through the use of dopants²⁴⁻³³ and surface modification,^{12,20,34-37} among others). Still, full understanding of their complex functional behavior is hindered by their microstructural complexity mainly because Li-rich oxides unavoidably crystallize with significant amounts of stacking faults.³⁸⁻⁴³ Li_2MnO_3 , the end member of this family of materials, represents an

excellent model material for understanding the microstructural complexity of this family. Li_2MnO_3 is known to crystallize in a $C2/m$ unit cell with alternation of layers with pure Li and Li/Mn atoms exhibiting a honeycomb like ordering (see Figure 1 (a)). The ideal structure of this compound exhibits three different lithium atomic positions; two of them located in the lithium layers (Wyckoff positions $2c$ and $4h$) and one corresponding to the lithium in the transition metal layer (Wyckoff position $2b$), as shown in the local environments represented in Figure 1 (b-d) respectively.

Figure 1: (a) Structure of Li_2MnO_3 where the different crystallographic sites of lithium are shown. (b-d) Local environment of each crystallographically different lithium site.

As in all Li-rich materials, stacking faults resulting from planar shifts of the mixed Li/Mn layer are energetically favorable although their extent strongly depends on the synthesis conditions (precursors, temperature and time).^{38,39,42,43} These stacking faults can be detected by different characterization techniques such as XRD,^{42,43} transmission electron microscopy (TEM)^{39,40} or solid state NMR,^{44,45} although their quantification has generally represented a challenging task. Bréger et al. used DiFFaX⁴⁶ simulations to model XRD data to qualitatively analyze stacking faults frequency in Li_2MnO_3 .⁴⁴ They also showed that defects strongly modify its NMR spectrum, although additional resonances were not assigned. In a more re-

cent work, the assignment of extra ^{17}O solid state NMR resonances was done by Seymour et al. and the percentage of stacking faults was estimated from the ratio of intensities.⁴⁵ The acquisition and analysis of ^{17}O solid state NMR spectra is however challenging due to the low natural abundance of ^{17}O and due to the fact that the active center is usually directly bonded to the oxygen, causing signal broadening and large shifts.

The quantitative determination of stacking faults from powder diffraction data is now possible with the FAULTS software,⁴⁷⁻⁴⁹ which enables the refinement of experimental diffraction patterns. This approach has been successfully applied to several materials, including Li_2MnO_3 .^{42,50-53} The quantitative results obtained in a previous combined XRD and TEM study of Li_2MnO_3 samples exhibiting microstructural variability represent an excellent opportunity to endeavor the analysis and assignment of the ^6Li solid state NMR spectra of defective Li_2MnO_3 . Assisted by first-principles calculations, we provide here an explanation to how local environments alterations change the Fermi contact shift allowing the assignment of the different signals in the NMR spectra, correlating NMR shifts to microstructural features. The combination of the results obtained from different techniques allows achieving an accurate description of defects in Li-rich oxides, represent an excellent case study to discuss the suitability of each technique for their study and provide new pathways to understand the correlation between disorder and function.

Results and discussion

Experimental XRD patterns and NMR spectra

Three different Li_2MnO_3 samples (A, B and C) have been synthesized and their XRD patterns are shown in Figure 2 (a). The inset of the figure shows a zoom of the XRD patterns in the $2\theta_{Cu}$ range of $20-35^\circ$ where superstructure reflections arising from Li/Mn order manifest. Defect-free materials exhibit 5 superstructure peaks in this $2\theta_{Cu}$ range, while heavily faulted samples exhibit a single peak with a strongly asymmetric broadening commonly known as

Warren fall.⁵⁴ As expected from the synthesis conditions selected, the samples exhibit notable differences owing to their different microstructure. Sample A exhibits a negligible degree of stacking faults and therefore this sample is considered to be stacking faults free. According to the FAULTS refinement performed in a previous work,⁴² sample B contains a low amount of stacking faults (13%) and sample C a high amount (42%).

Figure 2 (b) shows the ^6Li solid state NMR spectra of samples A-C in the region of interest (the full spectra, from 4000 to -2000 ppm, are shown in Figure S1). The dominant interactions in the ^6Li solid state NMR spectra of paramagnetic Li_2MnO_3 are the Fermi contact shifts generated by the unpaired electron density transferred from the paramagnetic manganese metals into the ^6Li spins through hybridization of the Li-O-Mn bond. The size of this interaction is a function of the unpaired electron spin density transferred to the nucleus and this property is considered to be additive.⁵⁵⁻⁵⁹ The final Fermi interaction or paramagnetic shift observed in the NMR spectrum can be therefore theoretically estimated considering all the individual interactions, where the sign of the transfer can be positive or negative.⁵⁵ In a fully coordinated MnO_6 octahedron Li-O-Mn bonds at 90° have a positive net spin density transfer of 120-150 ppm, while the bonds at 180° induce a negative spin polarization of 60-125 ppm.⁵⁶ Figure 1 (b,c) shows that there are eight manganese atoms in the first coordination sphere of $\text{Li}2c$ and $\text{Li}4h$. Four of them are double bonded via a 90° Li-O-Mn angle and the other four are single bonded via a 180° Li-O-Mn angle. Assuming the additive nature of the Fermi contact interaction, the NMR signals of the lithium atoms in the lithium layer ($\text{Li}2c$ and $\text{Li}4h$) are expected to appear at around 750 ppm. On the other hand, as shown in Figure 1 (d), $\text{Li}2b$ is surrounded by six manganese atoms, which are linked by a double 90° Li-O-Mn bond. The $\text{Li}2b$ signal is therefore expected at around 1500 ppm in the NMR spectrum. In agreement with this, previous ^6Li and ^7Li NMR studies of Li_2MnO_3 assigned the two resonances at around 750 ppm to $\text{Li}2c$ and $\text{Li}4h$ and the third one at 1600-1800 ppm to $\text{Li}2b$ positions.^{6,44,55,60-63}

From the close inspection of the experimental ^6Li NMR spectra shown in Figure 2 (b) we

Figure 2: (a) XRD pattern of samples A, B and C ($\lambda_{Cu} = 1.54056 \text{ \AA}$). Superstructure peaks from the XRD pattern of the samples are shown as inset. (b) ^6Li solid state MAS-NMR spectra of samples A to C recorded at 50 kHz. Spectra are normalized with the area of the set of peaks at 750 ppm. The dashed red line shows the position for the experimental peaks from sample A.

observe that sample A indeed exhibits two main resonances at around 750 ppm related to Li2c and Li4h, while samples B and C, on the contrary, exhibit a higher number of overlapped signals in this region. These additional resonances are ascribed to the new lithium sites generated by stacking faults as previously reported by Bréger et al.⁴⁴ In turn, while a single

resonance is expected at around 1500 ppm for lithium ions in $\text{Li}2b$ positions, all three samples exhibit an asymmetric shape due to the presence of overlapped signals at higher ppm values.

In general, NMR experiments can be regarded as quantitative being the integral intensity under a particular signal directly proportional to its population in the sample. Nevertheless, in certain cases, quantification by solid state NMR might not be straightforward (but still possible).⁶⁴ This is for example the case for paramagnetic materials due to their large spectral window and broad resonances where pulse imperfections or distinct magic angle spinning (MAS) rotational sideband patterns should be carefully considered.⁶⁵ In addition, the extremely rapid longitudinal and transversal relaxation of the nuclear spins due to paramagnetic interactions could lead to undetectable resonances. However, the evaluation of similar ^6Li NMR signals ascribed to analogous lithium environments is feasible as in these cases the effects previously mentioned are approximately constant. The ratio between the clusters of signals at around 750 ppm and 1500 ppm corresponds to the percentage of lithium in lithium layers vs. lithium in manganese layers, and the ideal value should be 3 (two $\text{Li}4h$ and one $\text{Li}2c$ against $\text{Li}2b$). In our samples, the calculated ratios for samples B and C are similar (3.12 and 3.13 respectively) while it is larger for sample A (3.26), which suggests that sample A has a lower content of lithium ions in $\text{Li}2b$ position with respect to samples B and C. The long reaction time and the higher temperature used in the synthesis of sample A could entail some lithium evaporation which would not be detected from XRD analysis due to the weak scattering factor of lithium nor using other analytical techniques such as induced coupled plasma (ICP), as minor stoichiometry differences are under the detection limit.

Figure 3 (a-c) shows the deconvolution for samples A-C respectively. The fitted shift positions and relative populations are listed in Table S1. The NMR signal of sample A observed at 1500 ppm requires at least three resonances. In turn, the signals observed at 750 ppm can be described using two peaks. The intensity ratio of these two resonances is opposite to the theoretical relative population of $\text{Li}2c$ and $\text{Li}4h$. However, the ratio between

peaks 3 and 4 in samples B and C (which, as discussed below, are related to ideal Li_2c and Li_4h respectively) is close to the expected 1:2. This is indicative that the two resonances in sample A are the result of other overlapped signals with similar local environments.

Figure 3: ^6Li solid state MAS-NMR spectra deconvolution of samples A-C respectively (a-c). Blue curves correspond to the experimental spectra while red curves correspond to the calculated one. See experimental section and supplementary information for deconvolution details.

Similarly, samples B and C could neither be properly described using the ideal number of resonances, and the peaks centered at 1500 ppm were also deconvoluted considering three

different components. The signals centered at 750 ppm required at least five peaks for a proper deconvolution, as shown in Figure 3 (b,c). In this case, the extra peaks can be attributed to stacking faults. This is further confirmed by the fact that the positions of the shifts are similar for both samples. The relative intensities of peaks 3 and 4 become smaller as the degree of stacking faults increases, while signals 1, 2 and 5 grow. Therefore we assign peaks 3 and 4 to the ideal stacking environments and resonances 1, 2 and 5 to the new Li environments generated by the stacking faults.

Simulated effect of stacking faults in the ^6Li NMR spectra

The use of DFT calculations is generally crucial for the assignment of subtle local environment changes like defects on NMR shifts. Computed Fermi contact shifts of ideal and structures with stacking faults are here examined to get further insight into the nature of the shifts originated by defects in the NMR spectra of Figure 2 (b). Three different structures have been built and are shown in Figure 4 together with their computed ^6Li NMR shifts.

Figure 4: ^6Li NMR spectra simulation of (a) ideal, (b) structure with isolated stacking fault and (c) structure with consecutive stacking faults. The dashed red lines show the position for the simulated ideal peaks for Li2b, Li2c and Li4h. The insets show a reconstruction of the simulated structures with additional atoms in the ab plane for a better observation of stacking faults.

In order to use the same cell size in all three cases, a 6-fold along the c axis supercell of the primitive unit cell has been generated with pymatgen.⁶⁶ These correspond to (a) an ideal structure with no stacking faults, (b) a structure with a single isolated stacking fault corresponding to a consecutive displacement of $(1/3, -1/3, 0)$ of all the layers above the stacking fault and (c) a highly faulted structure with several alternate layer displacements of $(1/3, -1/3, 0)$ or $(-1/3, 1/3, 0)$. The ideal structure (Figure 4 (a)) exhibits, as expected, three signals in agreement with the assignments of Figure 3 and previous reports,^{6,44,55,60–63} while the presence of stacking faults in Li_2MnO_3 splits the three main resonances of the ideal structure into additional signals (Figure 4 (b,c)). The average calculated shifts of the simulated structures are shown in Table 1, together with average experimental peak positions for comparison. In the simulated structures, the signals of $\text{Li}2b$ and $\text{Li}2c$ of the defective structures are gradually displaced to higher ppm values with increasing amounts of stacking faults. On the contrary, $\text{Li}4h$ exhibits additional signals at both lower and higher shifts, resulting in an average position that remains almost unmodified. These results agree well with the experimental patterns shown in Table 1 and in Figure 3, where the same trend is found.

Table 1: Computed and experimental average ^6Li NMR shifts. The latter correspond to the deconvolution using one peak per signal. The values in parenthesis correspond to the difference with respect to the ideal signal (for the case of the simulated shifts) or to sample A (for samples B and C).

Computed	$\text{Li}2b$ (ppm)	$\text{Li}2c$ (ppm)	$\text{Li}4h$ (ppm)
Ideal	1342	719	675
Isolated SF	1355 (+13)	738 (+19)	679 (+4)
Consecutive SF	1377 (+35)	760 (+41)	681 (+6)
Experimental	$\text{Li}2b$ (ppm)	$\text{Li}2c$ (ppm)	$\text{Li}4h$ (ppm)
A	1499	762	747
B	1506 (+7)	772 (+10)	750 (+3)
C	1511 (+12)	787 (+25)	747 (+0)

Simulated effect of vacancies and substitutions in the ^6Li NMR spectra

The combination of FAULTS refined XRD, NMR and DFT techniques has allowed assigning to relate the extra peaks shown in the spectra of samples B and C in Figure 3 to new environments created by stacking faults. The extra peaks of sample A, however, cannot be explained with planar defects (absence of Warren fall in the XRD pattern). On one hand, the peak at 1500 ppm shows at least three different environments. On the other hand, even if the peak at 750 ppm of sample A is deconvoluted using two peaks, their intensity ratio is opposite to the ideal one for $\text{Li}2c:\text{Li}4h$ (2:1 instead of 1:2) which suggests that additional overlapped peaks caused by other unknown structural defects should be considered. In the following section different microstructural defects are simulated to identify the origin of such extra peaks: i) Li^+/H^+ exchange, ii) lithium vacancies, iii) oxygen vacancies and iv) Li_2O vacancies.

Li^+/H^+ exchange

Figure 5: ^6Li NMR spectra simulation of $\text{Li}_{1.96}\text{H}_{0.04}\text{MnO}_3$ with Li^+/H^+ exchange in (a) $\text{Li}2b$, (b) $\text{Li}2c$ and (c) $\text{Li}4h$ positions. The dashed red lines show the position for the ideal peaks. The insets show the local environment where the proton (the small black sphere) is present, not the whole computed structure.

As previously mentioned sample A exhibits a lower content of lithium ions in $\text{Li}2b$ position with respect to samples B and C. A first scenario where the Li^+ are replaced by H^+ from moisture has been considered. Li^+/H^+ exchange has been reported to occur in acidic medium as well as when electrochemically oxidized in non aqueous electrolyte.^{67–71} Figure 5 shows the computed NMR corresponding to a material with $\text{Li}_{1.96}\text{H}_{0.04}\text{MnO}_3$ formula. Strikingly, less than 2% of hydrogen severely modifies the local environments which makes the NMR signals appear at much higher ppm than the one calculated for ideal Li_2MnO_3 . We believe that such difference arises from the fact that in the calculated relaxed structure hydrogen atoms are displaced from the center of the octahedron. As a consequence, the density charge of the oxygen atoms is severely modified and this is spread further away. Although the possibility of having a lower amount of Li^+/H^+ defects in the experimental spectrum is plausible, from the comparison of the NMR spectra in Figure 3 and the simulated one in Figure 5 we believe these defects are unlikely to exist in our material.

Lithium vacancies

Figure 6: ^6Li NMR spectra simulation of $\text{Li}_{1.96}\text{MnO}_3$ with lithium vacancies on positions (a) $\text{Li}4h$, (b) $\text{Li}2c$ and (c) $\text{Li}2b$. The dashed red lines show the positions for the ideal peaks. The insets show the local environment where the lithium vacancy (marked with a gray sphere) is present, not the whole computed structure.

A second scenario to account for lithium deficiencies in sample A would be that the high synthesis temperatures generate lithium vacancies that are charge compensated via electron hole formation in oxygen atoms, as proposed to occur during the charge process.⁷²⁻⁷⁵

In order to evaluate the impact of how lithium vacancies modify in the NMR spectra a single isolated lithium atom is removed from the structure and its total energy is calculated. Lithium is removed from its three crystallographic positions (*2b*, *2c* and *4h*) and the calculated total energy is the same in all cases. Therefore, it can be concluded that any of these three lithium defect structures would be equally likely to occur. As seen in Figure 6 (a-c) lithium vacancies increase the NMR shifts for all the crystallographic lithium positions. Even if the presence of electron holes has only been proposed to occur after electrochemical oxidation,^{72,74} this kind of defect cannot be totally discarded in the pristine sample as they can overlap with the main signal.

Oxygen vacancies

Figure 7: ${}^6\text{Li}$ NMR spectra simulation of $\text{Li}_2\text{MnO}_{2.96}$ with oxygen vacancies on positions (a) $4i$ and (b) $8j$. The dashed red lines show the positions for the ideal peaks. The insets show the local environment where the oxygen vacancy (marked with a gray sphere) is present, not the whole computed structure.

Reductive atmospheres have been used by some groups to synthesize oxygen vacant

structures.^{76,77} These generate Mn^{III} ions which improve the conductivity, enhancing charge-transfer ability and electrochemical performances.⁷⁶⁻⁷⁸ The experimental detection and quantification of such vacancies would be very interesting and useful to support these synthetic efforts. Oxygen vacancies in both $\text{O}4i$ and $\text{O}8j$ positions were considered and the resultant spectra are shown in Figure 7. In both cases the average formula unit of the computed structure is $\text{Li}_2\text{MnO}_{2.96}$. Oxygen vacancies are found to severely modify the local environment changing the spin transfer mechanisms and thus, generating a large set of new peaks. In addition to the resonances close to ideal signals (shown with a dashed red line), some additional peaks appear in the range 1000-1250 ppm and 0-200 ppm. These peaks are not observed in our experimental NMR spectra (Figure 2 and Figure S1) and again, even if differences between the simulated defect concentration and the experimental one should be considered, the presence of oxygen vacancies in our material can be ruled out because the extra peaks would still be present. The absence of a reducing atmosphere in our synthesis of the material further supports this result.

Li_2O vacancies

Finally, the combination of lithium and oxygen removal with the loss of Li_2O has been considered. It is well established that Li_2O removal upon electrochemical oxidation occurs.^{16,20,68,69,79-85} In agreement with previous reports⁸⁶⁻⁸⁸ we have found that the removal of $\text{O}8j$ is more energetically favored with an energy difference close to 20 meV per formula unit, while lithium atoms close to the oxygen vacancy are the most energetically favored, especially those with a $\text{Li}4h$ -vac.- $\text{Li}2b$ 180° configuration (see supplementary information and Figure S2). The NMR simulation corresponding to the most stable $\text{Li}_{1.92}\text{MnO}_{2.96}$ structure is shown in Figure 8. The removal of two lithium and one oxygen atoms generate a slight shift of $\text{Li}2c$ and $\text{Li}4h$ signals to higher ppm values, and a number of new signals around all ideal positions. The lower ppm shift of the two isolated peaks on the right part of the spectra are the consequence of lithium atoms with an oxygen vacancy in their octahedron.

Figure 8: ${}^6\text{Li}$ NMR spectra simulation of $\text{Li}_{1.92}\text{MnO}_{2.96}$ with $\text{Li}4h$, $\text{Li}2b$ and $\text{O}8j$ vacancies. The dashed red line shows the position for the ideal peaks. The inset shows the local environment where the Li_2O vacancy (marked with gray spheres) is present, not the whole computed structure.

Consequently, the transferred spin density is smaller. Simulations including the ideal and new $\text{Li}2b$ environments are able to reproduce the asymmetric lineshape found experimentally, except for the two peaks at 500-600 ppm. These could overlap with the main peak at 750 ppm and that are the consequence of 5-coordinated lithium atoms whose transferred spin density is reduced with respect to ideal 6-coordinated lithium atoms.

Discussion

The ${}^6\text{Li}$ NMR spectra of three samples with varying degree of planar defects have been compared. Assisted by DFT calculations, it has been confirmed that while ideal Li_2MnO_3 exhibits three ${}^6\text{Li}$ NMR signals (one per each different lithium site), stacking faults generate a higher number of overlapped signals. As a consequence, a displacement to higher shifts of the signals of $\text{Li}2b$ and $\text{Li}2c$ is observed, while the average position for the signal of $\text{Li}4h$ is maintained constant. This behavior is experimentally reproduced when comparing samples with low and high degree of stacking faults.

Peaks 1 and 2 and 5 from the deconvolution of the peak at 750 ppm in Figure 3 (b,c) are related to the new environments generated by the stacking faults. The sum of these new lithium environments can thus be used to quantify the degree of stacking faults as previously done by Seymour et al. using ^{17}O NMR data.⁴⁵ In this work it is considered that stacking faults modify oxygen environments in the faulted layer and the adjacent ones, and therefore the number of modified environments should be three times the degree of stacking faults. Nevertheless, if stacking faults are consecutive, the number of modified environments will be lower, as the effects of consecutive defects will overlap. Note that the same ratio will be found for lithium environments. In this case, the number of modified lithium environments will range from 1 (for 100% consecutive stacking faults) to 3 (for 100% isolated stacking faults) as seen in supplementary information and Figure S3.

Table 2: Degree of stacking faults (SF) obtained with FAULTS program from XRD data and number of modified lithium environments obtained from the NMR peak fitting.

Sample	SF (XRD) (%) ⁴²	Mod. Li env. (NMR) (%)	Ratio
A	None	None	None
B	13	21	1.6
C	42	57	1.4

Table 2 shows the comparison of the degree of stacking faults obtained by XRD using the FAULTS software,⁴² the sum of the percentage of new lithium environments measured by NMR and their ratio. In our study it is found that in samples B and C stacking faults are not isolated, which is in accordance with previous TEM observations.⁴² It should be noted that in highly faulted samples the probabilities of finding isolated stacking faults is strongly reduced.

Besides, even if the sample without stacking faults can be deconvoluted using two resonances, their intensity distribution does not correspond to the expected one. It has been thus concluded that other types of defects must be present and a deeper study to elucidate the origin of such deviation has been performed. The effect of Li^+/H^+ exchange and lithium, oxygen and Li_2O vacancies in the NMR shifts have been simulated. On the one hand, DFT

calculated spectra show that single oxygen vacancies and Li^+/H^+ exchange generate shifts which are clearly not present in our samples. On the other hand, both lithium and Li_2O vacancies result in new environments and shifts to higher ppms that could be in agreement with our experimental data. However, the shifts obtained for lithium vacancies appear more isolated, which is why we believe that overall Li_2O vacancies better reproduce the experimental spectrum of sample A. The strong overlapping of the different NMR signals coupled to the low amount of these defects (as they were not detected by XRD) hinders their quantification. The dominant effect of stacking faults in the spectra of samples B and C neither allows assessing the presence of Li_2O vacancies in their structure, although a lesser extent is expected (if any) from the different synthesis conditions used to prepare these samples.

These results illustrate that the quantification of stacking faults from NMR data is only possible in samples where stacking faults appear as isolated defects, which is not the case here. However, the combination of XRD and NMR results can be used to estimate the trend of stacking faults to locally concentrate. Finally, while XRD can give us quantitative information about the degree of stacking faults, NMR is highly sensitive to other defects that are undetected by other techniques such as XRD or ICP. The decoupling of different types of defects and their quantification by ^6Li NMR however remains a challenge.

Conclusions

In this work the NMR spectra of three different Li_2MnO_3 samples have been elucidated with the help of DFT and XRD data. Samples prepared at 900 °C were found to mainly exhibit stacking faults resulting in additional peaks in their NMR spectra. DFT calculations have accurately reproduced the peak assignment of the ideal structure and structures with stacking faults. Their quantification by ^6Li NMR is only possible if these are isolated, however, the comparison of the number of modified environments with XRD results can be used to characterize their trend to locally concentrate. From XRD data it was concluded

that the sample prepared at 1000 °C was stacking faults-free, but a close inspection of its NMR spectrum suggested other structural defects instead. DFT calculations were used to discriminate between Li^+/H^+ exchange and lithium, oxygen and Li_2O vacancies, being the latter the scenario that could best reproduce the additional NMR features. While XRD gives accurate information about the degree of stacking faults, NMR is shown to be highly sensitive to other microstructural defects which are not easily detected with XRD. Both techniques are thus complementary and combined provide an accurate description of the microstructural complexities Li_2MnO_3 can exhibit. The combined XRD/NMR/DFT methodology described in this work is expected to be extremely useful for describing defect structures in a range of technologically relevant paramagnetic solids.

Experimental section

Material synthesis.

Mixtures of Li_2CO_3 and the Mn precursor (MnO or MnCO_3) were ball-milled for 5 minutes (SPEX SamplerPrep 8000 M Mixer/Mill) in a Li:Mn ratio 2.04:1. The lithium excess is to compensate its loss occurring during the heat treatment at high temperature. The mixture was then pelletized in a 1 cm diameter pellet with a pressure of 5 tones for 1 minute and submitted to a two-step heat treatment in air; the first one for 5 hours at 500 °C and the second one with varying time and temperature. In our previous work the choice of Mn precursors was shown to be key to control the amount of defects in Li_2MnO_3 samples prepared by solid state reactions.⁴² Here, we study two samples prepared under the same conditions of temperature and time (900 °C for 5 hours) but using two different precursors (sample B using MnO and sample C using MnCO_3) plus a third sample (sample A) that is prepared with MnO and calcined at 1000 °C for 72 hours are studied. The use of MnCO_3 (sample C) results in a sample with a large amount of stacking faults, while the use of MnO allows considerably reducing their amount (sample B) and even suppressing them using long annealing times

and higher temperature (sample A).

Sample characterization.

All patterns were recorded on a Bruker D8 Discover instrument using monochromatic copper radiation ($\text{Cu K}\alpha_1$ $\lambda = 1.54056 \text{ \AA}$). Patterns were measured in a 2θ range of $15\text{--}110^\circ$ with a step size of 0.01° and a time per step of 1.550 s. Representations and analyses of the crystal structures were done using the VESTA program.^{89–91}

^6Li MAS solid state NMR experiments were performed on a Bruker 300WB spectrometer charged to a field of 4.69 T equipped with a 1.3 mm MAS probe. The samples were prepared in air. Spinning frequencies were set to 50 kHz in all cases. A rotor synchronized spin-echo pulse sequence ($90^\circ\text{--}\tau\text{--}180^\circ$ τ_1 acquisition) was used with typical 90° and 180° pulses of 1.3 and 2.6 μs , respectively. A recycle delay of 0.5 s was used and around 165 k scans were typically acquired in a ^6Li NMR experiment. The spectra were referenced to a 1 M solution of LiCl. The spectra were fitted using the Dmfit software.⁹² A summary of the fitting parameters can be found in Table S2. Magnetic measurements were done using a Quantum Design Physical Property Measurement System (PPMS) from 2.5–333 K.

Computational details.

The total energy and ^6Li NMR shifts for the different structures have been calculated using the Vienna Ab-initio Simulation Package (VASP).^{93,94} As in this work we aim to model diluted defects in a paramagnetic material, the use of the VASP code (plane waves and PAW potentials) is preferred to that of the more computer-demanding “all-electron” WIEN2k (FP-FLAPW) code,⁹⁵ as it allows to consider large supercells. In a previous study the comparison of Fermi contact shifts computed by the two approaches in several polyanionic battery materials showed that for compounds with transition metal ions exhibiting only t_{2g} electrons, the PAW method as implemented in VASP is as accurate as the FP-LAPW one.⁵⁹ Spin-polarized DFT calculations were performed and projector augmented wave potentials⁹⁴ were used to replace core electrons, whereas Li (2s), Mn (3p, 3d, 4s) and O (2s, 2p) valence electrons were expanded in plane-waves with a cut off energy of 600 eV. The Perdew-Burke-

Ernzerhof (PBE)⁹⁶ exchange-correlation function was used together with a Monkhorst-Pack grid. While the unit cell was obtained from XRD, atomic positions were relaxed with a residual force threshold of 0.02 eV Å⁻¹. The generalized gradient approximation with the Hubbard parameter correction (GGA+U) of Dudarev *et al.*⁹⁷ was employed. As it is shown in the supplementary information (Figure S4), a U value of 3.9 eV and the unit cell values obtained from the experimental refinement of XRD data of sample A ($a = 4.927(3)$ Å, $b = 8.523(3)$ Å, $c = 5.024(2)$ Å and $\beta = 109.39(3)^\circ$) result in the best agreement with experimental ⁶Li chemical shifts for Li₂MnO₃. A convergence of the total energy close to 0.5 meV per formula unit was achieved with these parameters. The atomic positions were allowed to vary while the unit cell size was maintained fixed. The total energy and NMR shifts of different Li₂MnO₃ stacking sequences were calculated using a representative amount of k-points. Supercells were constructed with the experimental values, using pymatgen tool.⁶⁶ The steps for the Fermi contact interaction calculation are shown in the supplementary information and Figure S5.

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Supporting Information Available

The following files are available free of charge.

- Full ^6Li solid state NMR spectra, deconvoluted experimental data, Li_2O vacancy selection, comparison of stacking faults, choice of U value and unit cell size, Fermi contact interaction calculation and technical NMR deconvolution fitting parameters.

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Graphical TOC Entry

In this work how an in-depth combination of XRD and solid-state NMR analyses can provide a very accurate qualitative and quantitative description of the defects present in Li_2MnO_3 is shown, ranging from the atomistic point of view of NMR and DFT to the long-range structural characterization of XRD supported by the FAULTS diffraction refinement program.