

An NMR Investigation of Lithium Occupancy of Different Sites in the Oxide Superconductor LiTi_2O_4 and Related Compounds

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The changes in lithium site occupancy as LiTi_2O_4 changes phase through the spinel to ramsdellite solid state phase transition are monitored by a ^6Li NMR investigation of quenched samples, using magic angle spinning. Other lithium/titanium/oxygen compounds are studied as references for lithium environments. The $8a/16d$ 3:1 partition of lithium in $\text{Li}_4\text{Ti}_5\text{O}_{12}$ is confirmed quantitatively. Lithium is found in several environments as a function of quenching temperature, and we discuss the assignment of the NMR responses to these different environments. These NMR studies, along with diffraction measurements, confirm that the spinel to ramsdellite transition is indirect, with two phases of changing composition coexisting between the spinel and the ramsdellite LiTi_2O_4 forms. © 2000

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INTRODUCTION

The spinel lithium titanate, LiTi_2O_4 , was the first oxide superconductor to be discovered, albeit with a modest superconducting transition temperature of 13 K. More recently there has been interest in other transition metal oxides that superconduct, the so-called “high T_c ” copper oxides, based on the $3d^9$ ion on the copper site. One of the motivations for studying LiTi_2O_4 , then, is to investigate further a superconductor based on ions in the early part of the transition series. The valence of the ions on the titanium site is expected to be 3.5^+ , leaving one half of one electron per titanium site sitting in a $3d$ orbit. A further motivation stems from the burgeoning usage of spinel structures as electrodes in battery applications, with or without solid state electrolytes.

The spinel structure is an open, three-dimensional, framework based upon close-packed oxygen. LiTi_2O_4 is close to an ideal normal spinel with lithium occupying the tetrahedral sites $8a$ and the titanium occupying the octahedral sites $16d$. Depending on synthesis conditions, however, significant deviation from this ideal spinel structure is well known.

Typical defects include partial lithium occupancy of the $8a$ sites, lithium substitution on the $16d$ sites, and lithium occupancy of the interstitial $8b$ and $16c$ sites. The concentration of these defects is low and cannot be probed quantitatively by X-ray diffraction; even with neutron diffraction it can be probed with only limited accuracy.

The strategy of this research program was therefore designed to explore the lithium occupancy via NMR of the various sites, $8a$, $8b$, $16c$, and $16d$, in a quenching study. This was based on the process of taking a stoichiometric spinel up to a given temperature and then rapidly cooling it to room temperature by dropping the spinel powder wrapped in a metal foil into liquid-nitrogen-cooled copper shot. Initial cooling rates are greater than $100^\circ\text{C}/\text{min}$. We estimate that the powder reaches room temperature in much less than 10 s by this procedure. We hoped that at temperatures of around 800°C , some occupancy of all the various alternative sites was likely, and that, by varying the temperature before the quench, systematic trends would be revealed. We concentrated on the ^6Li nucleus, believing that this nucleus has resolution advantages over the ^7Li nucleus (1), although there is a penalty in sensitivity.

To help in identifying and assigning the different lithium resonances that we obtained we also looked at the lithium resonances in some other compounds of known structure. These were

(i) $\text{Li}_4\text{Ti}_5\text{O}_{12}$, a spinel where lithium is known to occupy both the $8a$ and the $16d$ sites (the formula can also be written $\text{Li}_{1.33}\text{Ti}_{1.66}\text{O}_4$);

(ii) $\text{Li}_2\text{Ti}_3\text{O}_7$, a ramsdellite structure (the formula can also be written $(\text{Li}_{0.86})_c(\text{Ti}_{1.715}\text{Li}_{0.285})_f\text{O}_4$, where c and f denote channel and framework sites, respectively) (2);

(iii) LiTi_2O_4 , ramsdellite, formed at the highest temperatures of our quenching studies.

Earlier NMR studies in the spinel LiTi_2O_4 have concentrated on analyzing the ^7Li response from the principal $8a$, tetrahedral, lithium site in the structure (3, 4) or on the $^{47,49}\text{Ti}$ NMR from the distorted octahedral sites (5).

A directly relevant neutron scattering study (6, 7) of the spinel to ramsdellite phase transition demonstrates that the



transition starts between 875 and 900°C and that it goes to completion between 925 and 950°C. A spinel phase and a ramsdellite phase coexist in equilibrium in the transition region, although the phases are suggested to change in composition across the temperature range. Susceptibility and μ SR studies at low temperature (6) show that the ramsdellite LiTi_2O_4 phase involves some form of magnetic order. Conductivity measurements (6) indicate semiconductor character.

EXPERIMENTAL

NMR experiments were undertaken on a Bruker MSL 500 spectrometer, with a magnetic field of 11.75 T at room temperature, using a DOTY MAS probe. Typical spinning speeds were 4 kHz. All shifts are referenced with respect to the lithium resonance in an aqueous solution of lithium chloride, although our secondary reference compound was the lithium titanate LiTi_2O_4 powder spinel enriched in ^6Li used in an earlier study (4), with a linewidth of about 60 Hz (MAS).

As a function of quench temperature, we measured the chemical (or Knight) shifts and the linewidths for all observable peaks in each sample. Some supplementary spin-lattice relaxation times were also measured. Within each batch of samples the starting material was common, i.e., a large amount of spinel LiTi_2O_4 was first made by standard procedure (6), from which the different samples were made by heating up again and then quenching from different temperatures.

The typical heat treatment for slow-cooled samples involved 20 h at about 850°C in flowing gas (5% H_2 /95% Ar), followed by the switch-off of the heating element in the furnace, giving an initial cooling rate of 10 to 15°C per min. The sample was then taken out of the furnace 1 h later. The one, almost pure, ramsdellite LiTi_2O_4 sample that we ran was prepared at 1000°C for 20 h in the same (5% H_2 /95% Ar) gas and then slow-cooled as above.

RESULTS

The principal ^6Li resonance in spinel lithium titanate occurs at $(-2.1 \pm 0.2 \text{ ppm})$. Such a peak occurs in all the slow-cooled samples. In different runs, with quasi-identical conditions of sample preparation, small differences in this dominant NMR line were observed. For example, the NMR parameters of this line for sample runs A, B, and C, are set out in Table 1.

Before setting out the data for the quenched samples we discuss briefly some measurements on related compounds. Ramsdellite LiTi_2O_4 gives a dominant ^6Li broad NMR line (280 Hz L. W.) at +11.4 ppm, having a spin-lattice time of $(600 \pm 100 \text{ ms})$. There is also a small ^6Li additional NMR response ($\sim 17\%$ of total integrated intensity), narrow

TABLE 1
The ^6Li NMR Data for Three Different, Slow-Cooled, Samples, Prepared in Quasi-Identical Fashion

	T_1 (S)	Linewidth (Hz)	Shift (ppm)
A	84	46	-2.3
B	111	81	-2.0
C	63	47	-2.0

Note. These are data for MAS spectra in a spectrometer where 1 ppm is equivalent to 76 Hz.

($\sim 150 \text{ Hz}$), with a shift of about -0.1 ppm . This line must be associated with an intermediate phase in the thermal transformation of LiTi_2O_4 from spinel to ramsdellite. The large shift at +11.4 ppm gives the impression that we are dealing with a magnetic phase. Corroboration of this supposition has been sought by susceptibility μ SR studies (6), with equivocal results; the system may be best described as showing some magnetic characteristics of anti-ferromagnetic type and others of paramagnetic type. The value +11.4 ppm is well outside the normal range of shifts for insulating lithium compounds (see Table 3) and there is evidence that ramsdellite LiTi_2O_4 is nonmetallic (6).

The doped spinel $\text{Li}_4\text{Ti}_5\text{O}_{12}$ shows a ^6Li NMR spectrum that is complex. Figure 1 shows the spectrum in a 95% enriched sample, and we also show a simulation of the spectrum using two gaussian lines. The best fit occurs when one gaussian has an integrated area of one-third of the other. The parameters of the gaussians used in the fit are shown in Table 2.

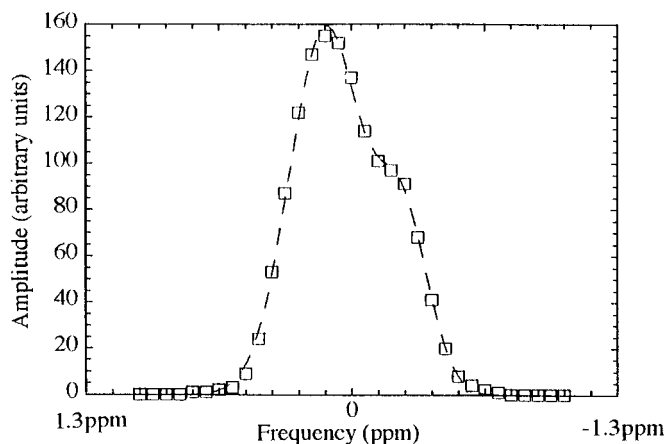


FIG. 1. A digitization of the experimental NMR spectrum (open squares) for ^6Li in isotopically enriched spinel LiTi_2O_4 under magic angle spinning, together with a two-gaussian theoretical fit (dashed curve). See Table 2 for the characteristics of the gaussians, one gaussian has three times the integrated area of the other; they are very slightly displaced with respect to each other, and they have different widths.

TABLE 2
The Parameters of the Two Gaussians Used to Produce the Fit Shown in Fig. 1

	Integrated area	Position (ppm)	Linewidth (Hz)
A	3	+0.1	36
B	1	-0.3	20

The split into two lines confirms the earlier data of Dalton *et al.* (4); we associate the more intense NMR line with the lithium nuclei on 8*a* sites, and the weaker line with lithium on the 16*d* (titanium) sites. The formula can be written Li_{1.33}Ti_{1.66}O₄, showing that, compared to LiTi₂O₄, the extra lithium corresponds to the shortage of titanium. Given that the structure remains spinel it is reasonable to surmise that the extra lithium in this nonmetallic compound goes into these vacant titanium sites.

Ramsdellite Li₂Ti₃O₇, definitely nonmagnetic, with the titanium ions in the 4⁺ state, shows a single narrow (120 Hz) Li NMR spectrum at 0.3 ppm with a T_1 of 2.0 ± 0.2 s. This is a surprisingly short T_1 for a nonmagnetic, nonmetallic, compound, and may well be associated with the fast-ion conductor status (8) of this material. The X-ray data (2, 8) indicates that there are two lithium sites, one in the channels of the structure and one in the framework, with lithium motion showing similar activation energies for both sites. Isotopic enrichment of such a sample, as above with Li₄Ti₅O₁₂, may be required to resolve the two different lithium sites that should be present.

For comparison purposes we include here some other chemical shift measurements in Li insulating compounds (Table 3).

The table illustrates first the narrow dispersion of lithium shifts in this type of compound. Second, since the first two compounds in the list have octahedrally coordinated lithium, while the others may have lower coordination, there is

TABLE 3
Chemical Shifts in a Range of Insulating Lithium Compounds

Compound	Shift (ppm)
LiNO ₃	-1.2
LiIO ₃	-0.1
Li ₂ SO ₄	-0.6
LiOH	+0.33
Li ₂ CO ₃ ^a	+1.2
LiBO ₂ ^a	+1.4
Li ₂ B ₄ O ₇ ^a	+0.3
Li ₂ MoO ₄ ^a	+1.2

^aFrom Ref. 1, where the reference is solid lithium chloride.

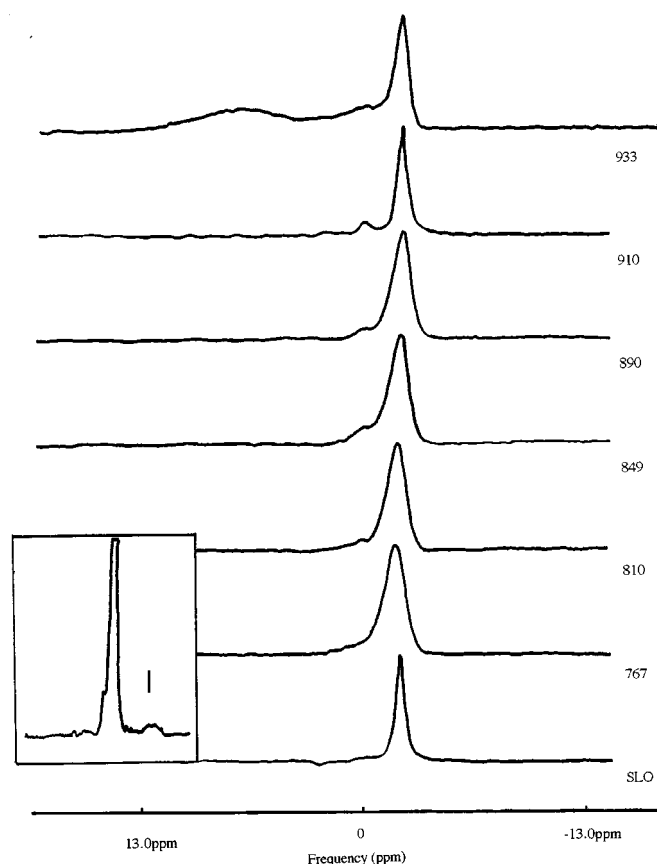


FIG. 2. The experimental ⁶Li NMR spectra for different quenching temperatures, marked in centigrade on the right of the spectra. The inset shows a typical spectrum enlarged by a factor of four, with a bar marking the spectral intensity that appears at around -10 ppm. The frequency scale is given by the presence of the large peak centered at -2.1 ppm together with the small peak at -10 ppm.

a trend such that increased coordination leads to upfield shifts.

We next present our data on the spinel LiTi₂O₄ subjected to different thermal quenching treatments. Figure 2 shows some representative ⁶Li spectra. We can unambiguously identify four ⁶Li responses:

- (i) the main spinel line at circa -2.1 ppm,
- (ii) a small line at around 0 ppm,
- (iii) the ramsdellite spectrum (the spectrum from the sample quenched from 933°C),
- (iv) and the fourth component, not very obvious on the main spectral sequence, but highlighted in the 4 times expansion shown in the inset (Fig. 2) where a distinct but small peak is discernable at about -10 ppm, marked by a bar above it.

There is also in most of the spectra some response at *circa* +3 ppm; this response is present even in the slowly-cooled samples and is difficult to phase, so that we ascribe it to impurities and/or an artifact of the experimental apparatus. It is not a 'quad echo.'

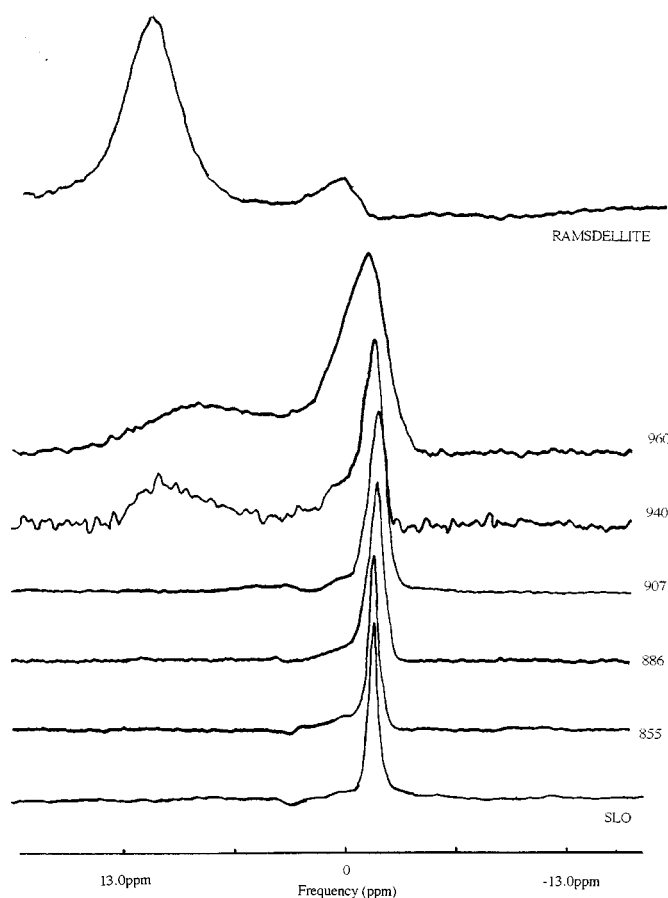


FIG. 3. As Fig. 2, but on a separate sample going to slightly higher temperatures. For comparison, at the top we show the spectrum for a sample that has been taken to the completion of the spinel to ramsdellite transition.

There are other features of the NMR response that we can see immediately in Fig. 2; for example the line from the slow-cooled sample is narrow, while for the quenched samples the NMR spectrum at the same shift is in general much broader. However, the line for the 910°C sample is narrower again. Figure 3 details a separate set of experiments on a new sample, exploring further the higher temperature range of quenched samples. We have also monitored the relative integrated areas of the NMR lines, proportional to the number of nuclei contributing.

Table 4 is a synopsis of the salient features of our experimental data:

In Table 4 columns 2 and 3 relate to the properties of the “spinel” line around -2 ppm. The problem of quantifying the intensity of the -10 line is severe since this line is broad, and the ${}^6\text{Li}$ NMR is noisy. Since this line is well-separated from the main spinel line at circa -2 ppm, some supplemental ${}^7\text{Li}$ NMR spectra have been taken to help with the absolute intensity of this line, column 4. The inset to Fig. 2

gives some idea how difficult it is to quantify column 4, Table 4, with any accuracy from ${}^6\text{Li}$ data alone.

We highlight several features of the data in Table 4:

(i) The shift value of the spinel line, column 2, remains invariant for different quenching temperatures, with one significant exception at 950°C where a clear increase to -1.5 ppm is observed. This shifted line is quite broad, column 3.

(ii) The linewidth, column 3, shows a general trend to larger values as the quenching temperature increases, but within this trend considerable fluctuations can occur, particularly close to the transition temperature from spinel to ramsdellite.

(iii) The integrated area of the -10 ppm line shows a peak near the 880°C quench temperature. This -10 ppm line, when it occurs, is broad and generally has a fast spin-lattice relaxation time of about 700 ms.

(vi) We do not show in Table 4 any quantification of the very small intensity that appears around 0 ppm. This line relaxes at the same rate as the adjacent -2.1 ppm spinel line. The relative integrated intensity of this 0 ppm line is estimated to be about 5% and appears to grow as the quenching temperature increases (see particularly Fig. 3). The 0 ppm line in the “pure” LiTi_2O_4 ramsdellite spectrum (Fig. 3, top) relaxes at a rate of 12 ± 4 s and comprises about 17% of the total ${}^6\text{Li}$ intensity.

(v) The ramsdellite LiTi_2O_4 line, a broad feature, appears at the $+6$ to $+12$ ppm position in the upper parts of Fig. 2 and 3, i.e., on the highest temperature data. The peak position appears to evolve as the quenching temperature varies. It relaxes quickly, at a rate of ~ 1.5 s $^{-1}$.

TABLE 4
Synopsis of the Salient Features of Our Experimental Data

Sample	Shift (ppm)	Linewidth (Hz)	Integrated line (-11 ppm) intensity as % of total
Slow*	-2.1	58	1
Q767	-2.1	103	0
Q810	-2.2	91	8
Q849	-2.2	99	10
Q890	-2.3	134	6
Q890	-2.2	85	10
Q910	-2.0	51	0
Q933	-2.4	66	0
Q855	-2.1	43	3
Q886	-2.3	72	5
Q907	-2.3	91	1.5
Q940	-2.1	107	3 ± 2
Q950	-1.5	240	3 ± 2

* The SLOW data are averaged over Table 1 data. The samples above Q855 involve the data presented in Fig. 2, while the data below Q933 are associated with Fig. 3.

DISCUSSION

The experiments illuminate the variability of lithium occupancy over the available sites. We attempt here to assign the different observed ^6Li responses to the possible sites in the crystal structure.

The rise in intensity, as quenching temperature rises, shown in both Fig. 2 and Fig. 3, near zero shift, culminating in Fig. 3 in a line (top spectrum) contributing 17% of the total ^6Li intensity, is possibly associated with an intermediate phase, mediating the spinel to ramsdellite transition. In the spectra we have observed that this phase never forms a dominant fraction of the NMR intensity but does represent a distinctly separate and different Li environment. It has to be admitted that the data is equally consistent with the appearance of a reduced oxygen phase still with spinel structure. Indeed, Gover *et al.* (7) in their neutron diffraction study find a two-phase region but no evidence for an intermediate phase; if the phase exists then it probably only ever exists at low concentration.

Supplementary X-ray diffraction measurements on a sample of composition LiTi_2O_4 , quenched from 910°C , indicated that the spinel component had a unit cell parameter close to 8.36 \AA (8.36 \AA is expected for $\text{Li}_4\text{Ti}_5\text{O}_{12}$) whilst the ramsdellite component has a unit cell close to that for the ramsdellite form of TiO_2 (10). This indicates that during the transformation from spinel to ramsdellite LiTi_2O_4 the spinel disproportionates into a lithium-rich spinel and a lithium-poor ramsdellite, consistent with neutron work showing a two-phase region involving the co-existence of ramsdellite and spinel phases (7) and with the current NMR study, which indicates that the intermediate contains a $\text{Li}_4\text{Ti}_5\text{O}_{12}$ -like phase (the small signal at around 0 ppm). As the temperature increases, the composition of the ramsdellite form, at least, changes, leading eventually to LiTi_2O_4 at the upper limit of the two-phase region.

The line at *circa* -10 ppm (Fig. 2, inset), corresponds to lithium sitting on octahedral sites in the metallic samples; it has a maximum in the Q849 and Q890 samples when 10% of the lithiums sit on these sites (Table 4). As we see from Table 3 such a large negative shift lies outside the range of possible shifts for insulating compounds, and it must represent a metallic Knight shift. As the ramsdellite begins to form, lithium moves away from these sites, as evidenced by the low occupancy for the Q910, Q933, Q940, and Q950 samples (Table 4).

In Ref. 3, we analyzed the shift and relaxation time for ^7Li in spinel LiTi_2O_4 , using the Korringa relation (9),

$$K^2 T_1 T = \{ \hbar / 4\pi k_B \} \{ \gamma_e / \gamma_n \}^2,$$

for the contribution to the shift and relaxation from *s*-wave conduction electrons, together with an appropriately modified, but analogous, relation for *d*-wave contributions. The

analysis led to the deduction that $K_s = -20$ ppm while $K_d = -22.4$ ppm, giving the net total shift of -2.4 ppm observed. Note the two almost cancelling contributions. A similar analysis here, using the net total shift of -10 ppm and the measured T_1 at room temperature of 700 ms, leads to $K_s = -100$ ppm with $K_d = -110$ ppm. Again we have the two almost cancelling contributions, with the individual components much larger, corroborating the assignment of this line to Li on a titanium site. It is the overlap of titanium-titanium wavefunctions that forms the conduction band in spinel LiTi_2O_4 , so a Li nucleus on a titanium site would be expected to be more closely connected to the conduction band, giving larger shift contributions. The main spinel line, associated with the tetrahedral site, has, in the SLOW sample, a shift of -2.1 ppm and a T_1 of 86 s at room temperature, fully consistent with earlier ^7Li data (4).

Moving now to the “+11” ppm line, the “ramsdellite” line, present in the three upper spectra of Fig. 3 and in the top spectrum of Fig. 2 (where it accounts for 18% of the total equilibrium ^6Li intensity), it is immediately clear that intensity within this broad line grows in a very inhomogeneous fashion with quenching temperature. For example, if we take the peak positions of this emerging line, at Q933 we get $+7$ ppm, at Q940 11 ppm, at Q950 about 8.8 ppm, finishing up at $+11.3$ ppm in the ramsdellite spectrum at the top of Fig. 3. This line is broad (~ 300 Hz, equivalent to 4 ppm) and fast-relaxing. The spectrum shows no signs of being the doublet that the hypothesis of two lithium sites would require (6). Again, Table 3 indicates that such large positive shifts are not normal for standard insulating, nonmagnetic, lithium compounds. Metallic character could account for such a large shift easily; however, Gover (6) has indicated that ceramic pellets of ramsdellite phase show no sign of metallic character. Taken with the large width of the MAS line, we believe that this NMR is corroborating suggestions of a magnetic structure (6), albeit rather weakly magnetic. Certainly if the lithium site were in close proximity to a large electronic magnetic moment in a paramagnetic phase then the spectrum would look very different to that observed; an ordered antiferromagnetic phase is more consistent with the NMR, but we need to do more measurements over a wide temperature range to elucidate this further.

We only see ramsdellite formation in NMR at quenching temperatures of greater than 933°C , whereas Gover *et al.* (7) observe the transition starting strongly at 900°C . However, as noted above, the initial ramsdellite formed is lithium-poor and may not be observable via NMR. In this context it is worth recording here that the first observation (11) of the spinel to ramsdellite transition in this system mentioned 950°C as the transition temperature. Subsequent single crystal growth of ramsdellite LiTi_2O_4 (12) used much higher temperatures $\sim 1100^\circ\text{C}$, using lithium metal and TiO_2 as the raw materials.

CONCLUSION

We have confirmed quantitatively the doublet structure of $\text{Li}_4\text{Ti}_5\text{O}_{12}$, with lithium occupying two sites in the expected ratio of 3:1. The chemical shift difference between the two lines is small.

We have explored the phase transition from spinel to ramsdellite via samples quenched from different temperatures. The NMR evidence, focused predominantly on chemical shift measurements, unveils a complex transition, consistent with phase disproportionation, where the majority of the lithium occurs in a lithium-rich spinel similar to $\text{Li}_4\text{Ti}_5\text{O}_{12}$. There is also the possibility that there is an intermediate phase mediating the transition. Ramsdellite LiTi_2O_4 exhibits a positive shift and fast spin-lattice relaxation; since conductivity measurements rule out any metallic character (6) this points to a magnetic phase, corroborating earlier μSR and susceptibility studies (6).

In the spinel metallic phase of LiTi_2O_4 , a small fraction of the lithium resides on octahedral sites; this fraction can rise to 10% of the total lithium for certain quenching conditions, but close to the ramsdellite phase transformation this fraction drops off again to close to zero.

The ramsdellite NMR line when the transition is complete is broad and situated at about +11 ppm, but during its growth, as the quenching temperature is varied, different parts of the line grow at different rates. This behavior may support the idea of at least two lithium sites in the ramsdel-

lite, one of which is preferentially occupied at lower temperatures.

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