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A ^7Li NMR study of the superconducting spinel $\text{Li}_{1+x}\text{Ti}_{2-x}\text{O}_4$

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Abstract. The superconducting oxide spinel system $\text{Li}_{1+x}\text{Ti}_{2-x}\text{O}_4$ ($0 \leq x \leq \frac{1}{3}$) has been studied in the temperature range 160–340 K by nuclear magnetic resonance (NMR) of the ^7Li nucleus. Elucidation of the two different Li sites (tetrahedral and octahedral) for $x > 0$ has been achieved via dilution of the ^7Li nuclei with ^6Li . NMR linewidths show a narrowing with increasing temperature for low x , indicating that the Li ions are becoming mobile around room temperature.

Observed chemical shifts show an increase at the metal–insulator transition, demonstrating that the Li nuclei act as weakly coupled probes of the bulk paramagnetic susceptibility. Analysis of these shifts, together with nuclear spin–lattice relaxation times, has allowed the Knight shift due to the Li(2s) contact to be calculated. This reveals that there is $\sim 7\%$ Li 2s character in the unpaired-electron wave function at the Fermi surface in LiTi_2O_4 .

1. Introduction

The discovery of superconductivity at high temperatures in cuprate systems has led to a flurry of research aimed at understanding the reasons for such novel electronic behaviour. In parallel with this, there has been a renewed interest in the older generation of non-cuprate oxide superconductors. One such compound is the spinel LiTi_2O_4 , which was first discovered to have a transition temperature (T_c) of ~ 11 K—the first superconductor with $T_c > 10$ K [1]. The metallic nature of this oxide can be understood in terms of direct overlap of Ti ($3d(t_{2g})$) orbitals across shared edges of TiO_6 octahedra. Photoemission and diffuse reflectance studies [2, 3], and electronic-structure calculations [4, 5], give support to the proposal that the conduction band is predominantly Ti($3d$) based and is located ~ 3 eV above the O($2p$) band. Specific-heat [6, 7] and magnetic-susceptibility measurements [7–9] give enhanced values of the density of states at the Fermi energy ($N(E_F)$) over that predicted from the band-structure calculations. Early conclusions about the superconductivity were that LiTi_2O_4 fitted well into a BCS description, being a weakly coupled d-band superconductor [6] with an electron–phonon coupling constant (λ_{e-ph}) of ~ 0.6 . More recently, the possible importance of electron–electron interactions in this material has been highlighted [5, 10], and Anderson has suggested that LiTi_2O_4 closely resembles candidate systems for the resonating-valence-bond (RVB) state [11]. A recent parallel Ti NMR study has discovered an unusually rapid spin–lattice relaxation of the Ti nuclei [12] suggesting that the electronic properties of LiTi_2O_4 are rather more complex than was first assumed.

It is possible to substitute additional Li for the Ti in LiTi_2O_4 , leading to the formation of a solid solution for $0 \leq x \leq \frac{1}{3}$ [13]. Such substitution leads to an increase in the

average oxidation state of the Ti present (effectively emptying the 3d band), limited at $x = \frac{1}{3}$ where all Ti is 4+, and, as would be expected, the system encompasses a metal–insulator transition at $x \sim 0.15$ [7, 9]. Initial studies of the nature of this metal–insulator transition by diffraction and susceptibility measurements [9] led the authors to believe that *the solid solution close to the transition region was inherently unstable, and that a spinodal disproportionation occurred, leading to the observed decrease in ‘superconducting volume fraction’ with x .* The results of a magnetoresistance study seem to indicate, however, that the system is indeed a solid solution [14]. A recent neutron-diffraction study has shown that the Li substitute directly and randomly for the Ti in the octahedral spinel B sites (16d) [15]; the nature of the metal–insulator transition may then be understood in terms of both the structural disorder (also recently evidenced by an EXAFS study [16]) and local electron-repulsion effects of the dopant Li, leading, eventually, to localization of the 3d electrons present [17, 18].

In a previous ^7Li NMR study of the metallic regime of the $\text{Li}_{1+x}\text{Ti}_{2-x}\text{O}_4$ system, Itoh *et al* [19] observed no significant Knight shift at the Li nucleus, and no change in the shift with x . They observed a decrease in NMR intensity per Li nucleus with increasing x , and concluded that octahedral Li (increasingly populated with increasing x) were invisible and nearest-neighbour tetrahedral Li were also ‘wiped out’ by their proximity to such B-site Li. These authors also measured the ^7Li spin–lattice relaxation as a function of temperature; results at high temperature (> 150 K) were consistent with a Korringa relaxation via conduction electrons. However, T_1 was seen to decrease significantly at lower temperatures, especially for samples close to the metal–insulator transition. This was attributed to an additional relaxation mechanism via paramagnetic impurities—localized Ti^{3+} moments. Such localized moments have usually been observed in samples in this system, and have been studied by EPR spectroscopy [20]. Recently, however, a preparative route has been developed that leads to samples with minimal concentrations of localized moments for $x \leq 0.1$, as evidenced by magnetic-susceptibility and EPR measurements [21], rendering them particularly attractive for a reinvestigation of the NMR properties in this system.

The results described in this paper are from NMR studies of the ^7Li in $\text{Li}_{1+x}\text{Ti}_{2-x}\text{O}_4$. We report (i) the resolution of signals from tetrahedral (8a) and octahedral (16d) sites via isotopic dilution, (ii) Li-ion mobility for samples in the metallic regime and (iii) a small but abrupt change in resonance shift at the metal–insulator transition, and relaxation behaviour that fits reasonably with a Korringa mechanism for metallic samples over the temperature range studied. The fascinating results of Ti NMR are to be reported elsewhere [12].

2. Experimental details

Single-phase samples of $\text{Li}_{1+x}\text{Ti}_{2-x}\text{O}_4$ were prepared via solid-state reaction of appropriate quantities of Li_2TiO_3 (corrected for Li deficiency), TiO_2 and Ti_2O_3 (corrected for O excess), as described elsewhere [14]. Purity and unit-cell parameters were confirmed by powder x-ray diffraction (XRD).

A sample of composition $x = \frac{1}{3}$, with significantly diluted ^7Li nuclei, was synthesized as outlined below. ^6Li -enriched metal (containing 5% ^7Li) was dissolved in water, and the carbonate was precipitated with 1 M Na_2CO_3 solution. The resulting $^{6,05}\text{Li}_2\text{CO}_3$ was dried, and then reacted with the appropriate quantity of TiO_2 at (i) 750 °C for 12 h and (ii) 850 °C for 24 h. Powder XRD showed the resulting spinel material to be single phase.

Magnetic-susceptibility measurements were performed on a superconducting quantum-interference device (SQUID) magnetometer (Quantum Design) at the Royal Institution. NMR

spectra were acquired between 160 and 340 K with magic-angle spinning (MAS) up to 12 kHz on a Bruker MSL 500 spectrometer at the University of St Andrews. All ${}^7\text{Li}$ chemical shifts were measured relative to a 1 M solution of LiCl .

3. Results and discussion

3.1. An elucidation of tetrahedral and octahedral Li resonances

The static, room-temperature spectra of ${}^7\text{Li}$ in the two end members ($x = 0$ and $x = \frac{1}{3}$) are compared in figure 1. As can be seen, there is no evidence of two discrete peaks for $x = \frac{1}{3}$. There are, however, significant differences in the linewidths and lineshapes. These are discussed below.

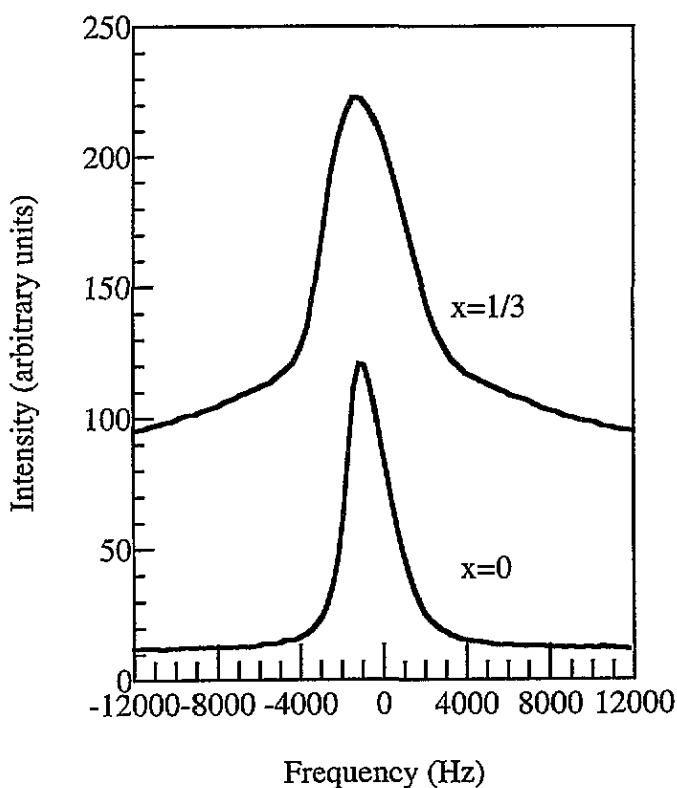


Figure 1. A comparison of the ${}^7\text{Li}$ NMR spectra of LiTi_2O_4 (bottom) and $\text{Li}_{1.33}\text{Ti}_{1.67}\text{O}_4$ (top).

3.1.1. LiTi_2O_4 . For $x = 0$, only tetrahedral Li is expected. The tetrahedral sites in the spinel structure have *cubic* local symmetry, and therefore no chemical-shift anisotropy or quadrupolar splitting is expected: the dominant source of line broadening should be through-space dipolar interactions between ${}^7\text{Li}$ nuclei.

The observed spectrum is symmetric, with a linewidth of 2.1 kHz (full width at half height) at room temperature. A rough calculation, based on the van Vleck second-moment

formula for powders [22] and a Gaussian lineshape, of the theoretical Li linewidth in LiTi_2O_4 produced a value of 2.2 kHz if the broadening effect of nearest-neighbour Li nuclei only was taken into account. This is clearly a lower limit: the O, Ti and non-next-nearest-neighbour nuclei will all contribute to raise this theoretical estimate.

3.1.2. $\text{Li}_{1.33}\text{Ti}_{1.67}\text{O}_4$. For the $x = \frac{1}{3}$ sample, both tetrahedral and octahedral Li are expected. The tetrahedral Li would be expected to experience similar broadening effects to those above, with the possibility of increased dipolar broadening due to the closer proximity of octahedral B-site Li ($d(\text{Li(A)}-\text{Li(B)}) = 3.49 \text{ \AA}$, cf $d(\text{Li(A)}-\text{Li(A)}) = 3.64 \text{ \AA}$ for $x = 0$).

The octahedral Li ought to display very different broadening effects. Firstly, the 'octahedral' site has an associated trigonal distortion due to the imperfect packing of the O [9]. This means that the local site symmetry is axial, so that both chemical-shift anisotropy and quadrupolar interactions are expected in addition to the dipolar interactions discussed above. Values of ^7Li quadrupolar coupling constants have been derived by Hon and Bray [23] for a number of Li compounds. Values range between 38 and 110 kHz, depending on the degree of asymmetry at the Li site. A further complication is caused by the random occupation of the B sites by Li and Ti. A given B-site Li^+ ion has six nearest-neighbour B-site cations. These six nearest neighbours may be any combination of Li and Ti (e.g. one Li and five Ti). Thus, there will be a range of octahedral Li with slightly different chemical shifts, dipolar and quadrupolar interactions. This will further broaden the spectrum for octahedral Li.

The observed static spectrum (figure 1) is consistent with the above predictions. The linewidth at half height is about 4.7 kHz—rather higher than for $x = 0$. The lineshape is very different, however, with a much broader base than for $x = 0$. It seems likely that the spectrum is a combination of signals from the two different sites: a reasonably sharp isotropic peak from the cubic tetrahedral sites superimposed upon a broad peak from the axial 'octahedral' sites.

The resolution of these two proposed signals was attempted using MAS. The linewidth was drastically reduced from ~ 4.7 kHz to ~ 300 Hz. The lineshape was symmetric: there was no evidence for the two expected signals. There are two possible explanations for this:

(i) the chemical shifts for octahedral and tetrahedral sites are so close that resolution is not possible, even with high-frequency MAS;

(ii) the octahedral Li are not observed (improbable considering the different lineshapes for $x = 0$ and $x = \frac{1}{3}$).

The second of these explanations was proposed by Itoh *et al*, who measured static spectra, and observed a decrease in ^7Li peak intensity for increasing x in $\text{Li}_{1+x}\text{Ti}_{2-x}\text{O}_4$ [19]. They explained this in terms of the lack of observation of octahedral Li nuclei plus those tetrahedral Li nuclei that happened to be adjacent to a B-site Li. The reason for such 'invisibility' was not understood.

In order to verify Itoh's result, peak intensities were integrated from both static and spun spectra for a number of samples. The results are plotted in figure 2, taken with a single-pulse acquisition sequence with a pulse width of 2.45 μs (set for $\pi/2$ in the $x = 0$ sample). This corresponds to a B_1 of about 60 G, or 100 kHz. Given the range of quadrupole coupling constants—cited earlier [23]—in Li compounds, it seems likely that our observation conditions are such that the RF irradiation is larger than the quadrupole splittings. This puts the experimental configuration close to the category of non-selective excitation [24–26].

Static intensities show a much smaller decrease in intensity per Li nucleus with increasing Li substitution than the loss observed by Itoh, corresponding at most to about $\frac{1}{3}$

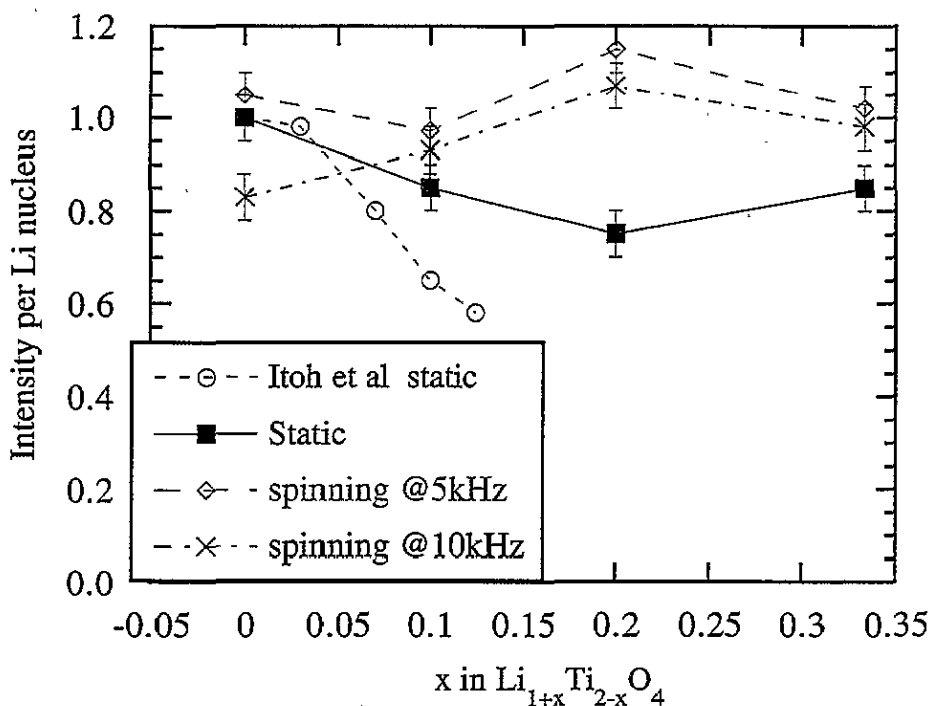


Figure 2. Measured signal intensities of $\text{Li}_{1+x}\text{Ti}_{2-x}\text{O}_4$. Data from Itoh *et al* [19] are included for comparison.

of the Li at $x = \frac{1}{3}$. This value is the same as the fraction of Li occupying the B sites, and is consistent with a 'wiping out' of the octahedral Li. However, spinning spectra showed a recovery of this 'lost' intensity to (within experimental error) the expected value for complete observation of all the Li. This implies that some intensity is missed on integrating static spectra—probably due to the very broad nature of the peak base for $x > 0$, together with some loss from quadrupolar satellites (subsequently brought back in by spinning). There is an anomalous result: the $x = 0$ sample spun at 10 kHz shows a substantial *reduction* in intensity from the static spectrum. This is probably an experimental effect caused by the increased loading of the RF coil by the metallic LiTi_2O_4 on spinning.

These intensity studies suggest that both Li sites are seen, and that the problem of separating the A- and B-site signals is one of chemical-shift resolution. The two sites are not resolved due to line-broadening effects, which are not removed by MAS. The main contribution to these is likely to be from interactions that have a different orientation dependence to those eliminated by MAS. One way to decrease these interactions is to increase the average distance between successive ${}^7\text{Li}$ nuclei since dipolar broadening is inversely proportional to the cube of the Li–Li separation. This effect can be brought about by reducing the concentration of the ${}^7\text{Li}$ isotope in the material. A ${}^6\text{Li}$ -enriched sample of $x = \frac{1}{3}$ was therefore synthesized, as described above.

A spectrum of ${}^7\text{Li}$ in ${}^{6.05}\text{Li}_{1.33}\text{Ti}_{1.67}\text{O}_4$ (MAS, 11 kHz) is illustrated in figure 3, and reveals just how successful this strategy was at distinguishing the two sites. The spectrum clearly shows at least two contributions to the lineshape. The overall linewidth (full width at half height) is 0.7 ppm (or ~ 130 Hz) compared with a spinning linewidth of ~ 300 Hz for the natural Li sample. The two chemical shifts, derived from fitting the observed spectrum

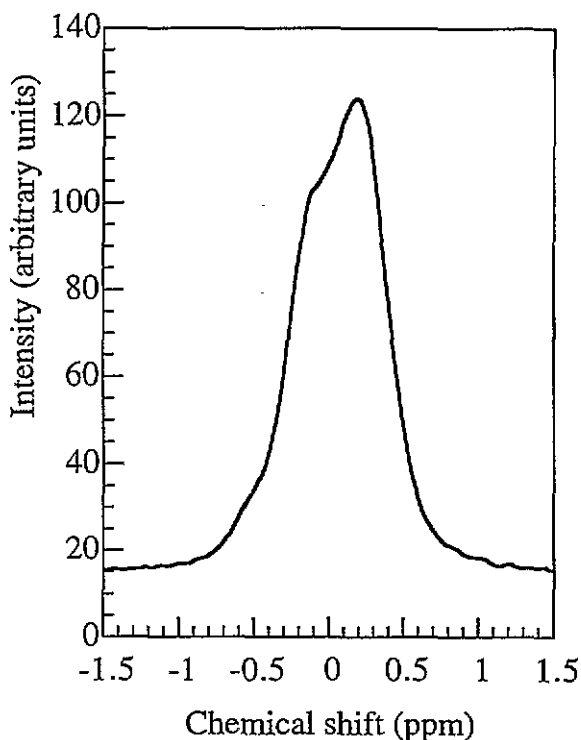


Figure 3. The ${}^7\text{Li}$ NMR spectrum of ${}^{6.05}\text{Li}_{1.33}\text{Ti}_{1.67}\text{O}_4$, demonstrating the elucidation of signals from both spinel cation sites.

to two Gaussians, are 0.20 and -0.09 ppm with respect to a 1 M solution of LiCl. In order to try to assign the two signals to their corresponding sites, the chemical shifts of some Li salts containing octahedral Li (LiNO_3 , Li_2SO_4 , LiIO_3) and one containing tetrahedral Li (Li_2S) was measured. The octahedral Li all showed $-0.6 < \delta < -0.1$ ppm, whereas the tetrahedral Li had $\delta = +2.4$ ppm. This suggests that the tetrahedral site may be the one with higher δ . The overall lineshape for this sample indicates that the peak at -0.09 ppm may be rather broader in nature than that at $+0.20$. This is consistent with the presence of a range of B-site Li with slightly different local environments, and supports the suggested assignment.

3.2. Evidence of Li mobility at room temperature from NMR line narrowing

Estimated values of spectral linewidths are plotted for all samples as a function of temperature in figure 4. The first point to note is the large linewidth of the $x = 0.2$ sample compared with that for $x = \frac{1}{3}$ (4.7 kHz, figure 1): this is probably due to the presence of localized Ti^{3+} (absent for $x = \frac{1}{3}$), leading to a greater range of ${}^7\text{Li}$ chemical shifts. For compositions with $x < 0.05$, a narrowing of the NMR spectrum is evident with increasing temperature, whereas for $x > 0.05$, no decrease in linewidth is observed. For $x = 0$, only tetrahedral Li is present, and the line broadening must be due to dipolar interactions between ${}^7\text{Li}$ nuclei. Hence, a reduction in linewidth with increasing temperature indicates a smaller dipolar effect. This could come about because of partial averaging of interactions through motion of the Li within the lattice. Therefore, the line narrowing must be caused

by motion of Li through the spinel structure: indeed, the possibility of room-temperature Li intercalation in LiTi_2O_4 [27] requires Li mobility. The narrowing effect is by no means total: the minimum linewidth is ~ 2 kHz, compared with a spinning linewidth of ~ 90 Hz. This implies that the Li are still very much restricted in their motion: the dipolar interactions are not averaged to the same extent as for MAS.

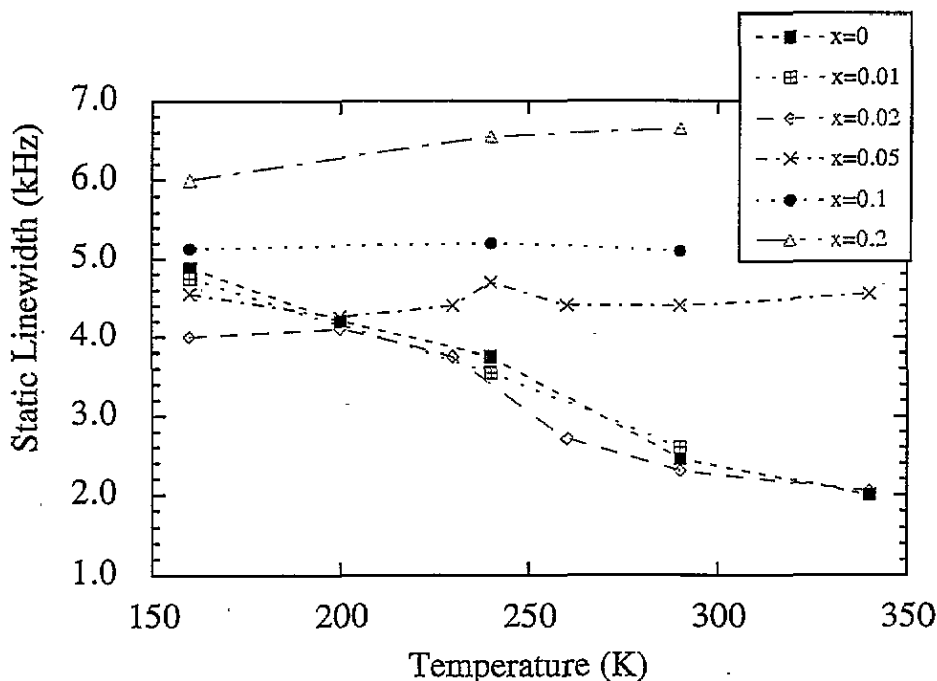


Figure 4. The static ${}^7\text{Li}$ NMR linewidth versus the temperature in $\text{Li}_{1+x}\text{Ti}_{2-x}\text{O}_4$.

The motion might be understood by the existence of Li vacancies in the tetrahedral A sites, as recently evidenced from a neutron-diffraction study, which revealed a 5–8% deficiency for all compositions [14]. The compositional influence on the Li mobility is interesting; an explanation for the observed behaviour is not obvious, but a possible factor is the strength of the Li–O bond, which would be expected to increase with x as the bond distance decreases [14].

3.3. Chemical shifts and magnetic susceptibility

The room-temperature shifts of ${}^7\text{Li}$ in $\text{Li}_{1+x}\text{Ti}_{2-x}\text{O}_4$ samples show an interesting change as the metal–insulator transition is traversed. These values were derived from spinning (10 kHz) spectra and plotted in figure 5.

If the Li nuclei were oblivious to the 3d electrons on the Ti sublattice, then one would expect the chemical shift to be higher for compositions with a greater proportion of tetrahedral Li (δ of tetrahedral Li is generally higher than that of octahedral—see the previous section). The observed trend is the opposite of this, indicating an *increase* in the shielding constant and therefore a reduction of the effective field around the nucleus. This

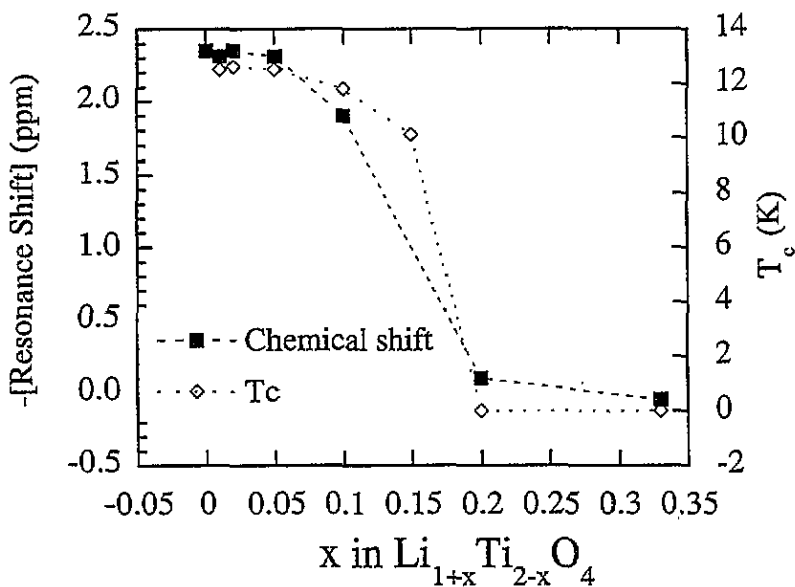


Figure 5. ${}^7\text{Li}$ resonance shifts in $\text{Li}_{1+x}\text{Ti}_{2-x}\text{O}_4$. The negative of the shift is plotted to demonstrate the correlation with the superconducting transition temperature (T_c).

has to be put down to the influence of the conduction electrons, which the Li nuclei are somehow sensing. The ${}^7\text{Li}$ in metallic compositions appear to be *shielded* with respect to those in insulating samples. This is probably a consequence of core polarization [28], where the spin state of the conduction electron in the highest, partially occupied orbital influences the effective radii of the two possible spin states in the Li s orbitals to different degrees, resulting in a field reduction.

It is interesting that the variation in shift is not linear with x —metallic compositions show $\delta \simeq -2.4$ and there is a change at the metal–insulator transition to $\delta \simeq 0$. The maximum shift for the metallic compositions represents only $\sim -1\%$ of the Knight shift of Li metal ($K_{\text{Li}} = 260$ ppm) [28], demonstrating that the Li present is almost purely ionic.

Values of magnetic susceptibility at 270 K are plotted against composition in figure 6(a). The full temperature profile for $x = 0.025$ is shown in figure 6(b) and demonstrates the minimal concentration of Curie-type localized moments in metallic samples.

The correlation between T_c and shift is excellent, though that between susceptibility and shift is less marked. Compositions on the insulating side of the metal–insulator transition have higher-than-expected values of susceptibility, presumably due to a large contribution from localized Ti^{3+} states. The ${}^7\text{Li}$ nuclei thus appear to be weakly coupled probes of the density of states of conduction electrons. A full analysis of the magnetic-susceptibility results together with EPR measurements across the solid solution will be published soon [21].

3.4. Nuclear spin-lattice relaxation

$t_1 T$ values are plotted against temperature for all samples studied in figure 7. Absolute values for metallic samples agree very well with those found by Itoh *et al* [19]. A room-temperature value for t_1 of 71 s ($t_1 T = 21\,000$ s K) was measured for $x = \frac{1}{3}$; the slow relaxation is a reflection of the absence of 3d electrons for this composition. Two trends are apparent from the data:

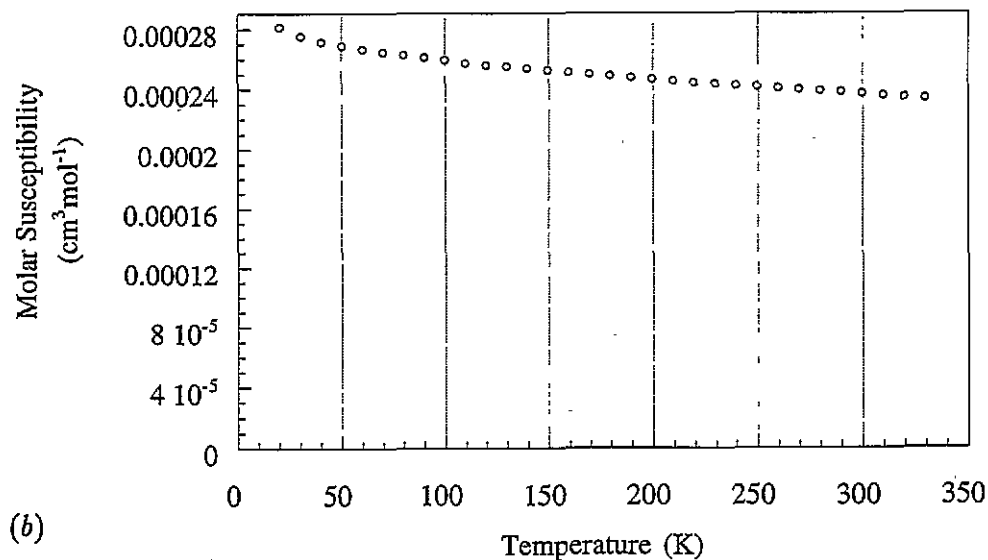
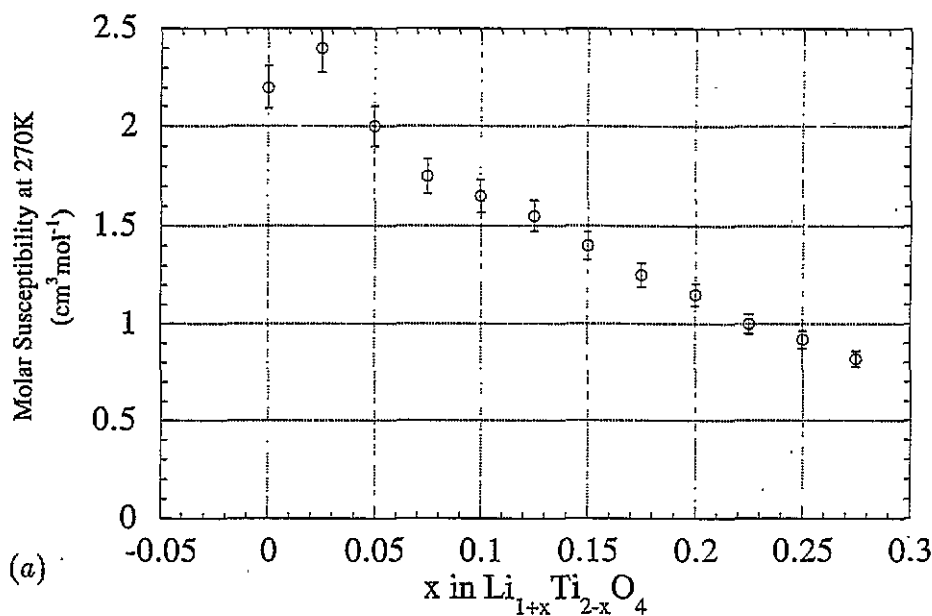


Figure 6. (a) The molar susceptibility at 270 K in $\text{Li}_{1+x}\text{Ti}_{2-x}\text{O}_4$. (b) The molar susceptibility versus the temperature for $\text{Li}_{1.025}\text{Ti}_{1.975}\text{O}_4$.

(i) there is a sharp drop in t_1 at the metal–insulator transition;

(ii) there is little temperature dependence of $t_1 T$ for metallic compositions, but a decrease is seen at the lowest temperature measured, the magnitude of which seems to scale with Li substitution.

The increase in relaxation efficiency for insulating samples in figure 7 (i.e. $x < \frac{1}{3}$) might be understood by a change in relaxation mechanism from interaction with conduction electrons (Korringa type [29]) to interaction with localized $3d^1$ moments, which increase substantially

in concentration at the metal-insulator transition. The observed slight decrease in t_1T for metallic compositions at low temperatures may also be due to a contribution from localized moments, though the magnetic susceptibility data make this seem somewhat unlikely. An alternative explanation is a change in the Knight shift with temperature ($K^2t_1T = \text{constant}$), though measurements indicate little change down to 160 K.

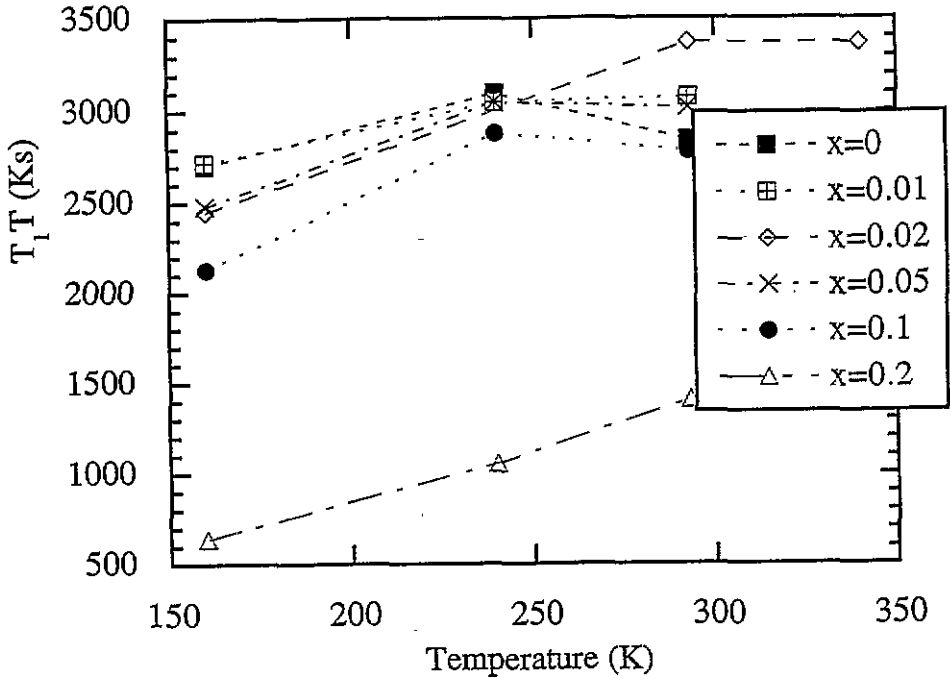


Figure 7. t_1T versus the temperature for ${}^7\text{Li}$ in $\text{Li}_{1+x}\text{Ti}_{2-x}\text{O}_4$.

The previous section demonstrated that the overall Knight shift (K_{obs}) for LiTi_2O_4 is negative, due to the dominating core-polarization term. If a Korringa mechanism is assumed at room temperature, then it is possible to deconvolute the contact (K_s) and core-polarization (K_{cp}) Knight shifts, using room-temperature t_1T values as below:

$$K_{\text{obs}} = K_s - K_{\text{cp}} \quad (|K_{\text{cp}}| > |K_s|) \quad (1)$$

$$K_s^2(Tt_{1(s)}) = (\hbar/4\pi k_B)(\gamma_e/\gamma_n)^2 = S = 1.6 \times 10^{-6} \quad (2)$$

$$K_{\text{cp}}^2(Tt_{1(\text{cp})}) = 2.5S = 8.0 \times 10^{-6} \quad (3)$$

$$1/t_{1(\text{obs})}T = 1/t_{1(s)}T + 1/t_{1(\text{cp})}T. \quad (4)$$

Here we adopt, in the Korringa relation for the core-polarization mechanism, a value of 2.5 for the orbital degeneracy factor [30]. Substituting (2) and (3) into (4), using (1) to substitute for K_{cp} , and solving the resulting quadratic in K_s leads to two solutions for K_s , only one of which is possible. The calculated value of LiTi_2O_4 at room temperature is 19.1 ppm (cf 260 ppm for Li metal), and corresponds to $\sim 7\%$ 2s character at the Li nucleus. This seems

to agree approximately with valence charges deduced from electron-structure calculations [5]. The derived value for LiTi_2O_4 is also consistent with those observed in another d¹-band system Na_xWO_3 [31]. A similar deconvolution of the 160 K data leads to the slightly higher K_s value of 19.9 ppm, indicating more s character, and may provide an explanation for the shorter-than-expected t_1 relative to the room-temperature data.

4. Summary

The ${}^7\text{Li}$ NMR studies of the $\text{Li}_{1+x}\text{Ti}_{2-x}\text{O}_4$ solid solution described above have provided a number of interesting results. The two crystallographically distinct Li sites have been resolved for $x = \frac{1}{3}$ by reducing dipolar broadening via isotopic dilution. Studies of spinning intensities indicate that all Li are observed, though static intensity is 'missed' for octahedral Li sites due to their non-cubic environment. Spectral line narrowing has been observed for $x < 0.05$, indicating that the Li are mobile at room temperature in these metallic samples. Resonance shifts, although extraordinarily small, display a correlation with superconducting transition temperature. A derived value of the Li(2s) Knight shift for LiTi_2O_4 is consistent with band-structure calculations. Relaxation measurements indicate Korringa behaviour at room temperature, but a second mechanism, whose origin is presently unknown, but is unlikely to be simple localized 3d¹ moments, comes into play below 160 K. We speculate that this may be due to a small change in Li s character in the Fermi-surface wave function.

Acknowledgments

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