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Titanium nuclear magnetic resonance in metallic superconducting lithium titanate and its lithium-substituted derivatives $Li_{1+x}Ti_{2-x}O_4$ $(0<x<0.10)$

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One of the first reported oxide superconductors lithium titanate $Li_{1+x}Ti_{2-x}O_4$ ($T_c \sim 12$ K for $0<x<0.10$) is studied here by nuclear magnetic resonance of the titanium nucleus (^{49}Ti and ^{47}Ti) in the temperature range 160–330 K. The study encompasses the temperature variation of the Knight-shift components and the quadrupole interaction for $LiTi_2O_4$ (the $x=0$ end member), the variation of the spectrum at room temperature as a function of x in the range $0<x<0.10$, and some preliminary measurements of the nuclear spin-lattice relaxation time. The samples have been well characterized by a combination of x-ray and neutron diffraction, and magnetic-susceptibility (superconducting quantum interference device ac inductance) measurements. A feature of the present samples is the very low density of localized moments in the metallic regime, as compared to previous studies of the same system. The results show strong broadening of the Ti spectrum induced by lithium substitution and fast relaxation. The isotropic and axial Knight-shift components and the quadrupole interaction in $LiTi_2O_4$ exhibit a strong temperature dependence. The isotropic Knight-shift component is linked to a temperature variation of the electron spin susceptibility χ, leading to an estimate of the average orbital susceptibility in the $x=0$ compound of 30×10^{-6} emu/mole, a value corroborated by theoretical calculations. The axial component of the shift indicates that both the orbital and the spin susceptibilities in the $x=0$ compound are highly anisotropic. The values of isotropic shift and χ indicate that the electronic system at $x=0$ is a narrow d-band metal with significant electron-electron interaction.

INTRODUCTION

The metallic spinel lithium titanate $LiTi_2O_4$ was discovered early on to exhibit a transition to a superconducting state at $T_c \sim 12-13$ K.[1] Its properties have excited more interest recently in the comparison between oxide superconductors involving electrons in nearly empty $3d$ shells and those involving electrons and holes in nearly full $3d$ shells (the copper-oxide-based systems). Early speculation here was that the ground state of the $3d^1$ systems might not involve antiferromagnetic (AF) order, but rather order of the resonating valence bond (RVB) type, as advanced by Anderson.[2] $LiTi_2O_4$, of course, has an electron occupation of the titanium band of $3d^{0.5}$; $3d^1$ occupancy would correspond to, say, $MgTi_2O_4$. The experiments described here therefore explore a $3d$ occupancy range somewhat away from the RVB position. [We note that there has been a recent publication[3] on the metal-nonmetal transition in a $3d^1$ system, $La_{1-x}Sr_xTiO_3$.] On the other hand, $LiTi_2O_4$ corresponds to an occupancy of one $3d$ electron per formula unit, so that there may be a possibility of similar ordering to a RVB.[4] Other intriguing aspects of this superconducting titanate system lie in the cubic spinel structure, which would produce its own particular constraints on the competition between the AF and RVB order, and the predicted t_{2g} character of the conduction-electron wave functions on the titanium site, such that the conduction band probably involves predominantly direct overlap between these wave functions with only minor oxygen hybridization. A metal-nonmetal transition occurs as the lithium substitution for titanium increases to about $x=0.15$.[5,6]

Studies of the properties of lithium titanate, and its variants with extra lithium substituted for titanium, have encompassed many techniques, spanning two decades. Recent studies, of direct relevance to this paper, include a neutron-diffraction study by Dalton *et al.*,[7] a ^7Li NMR study by Itoh *et al.*,[8] a muon-spin-resonance (μ^-SR) experiment by Nishida *et al.*,[9] and some work mainly on the specific heat by Heintz *et al.*[10] A NMR study of titanium metal by Ebert, Abart, and Voitlander[11] is also relevant. The neutron-diffraction work[7] has, among other things, investigated the dependence on x of the average trigonal distortion around the B sites (the octahedrally coordinated sites), finding that this distortion, which can be represented by a single parameter u (which takes the value of 0.375 in the ideal, nondistorted, structure), does not depend on x. This work also definitively identifies the location of the extra lithium ions, inserted for $x>0$, as the B site and further deduces that the distribution of

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these lithium ions is random.

In the NMR study[8] a reasonable account of the diminution of the ^{7}Li signal as x increased could only be made with the assumption that a lithium on a B site is not only unobservable, but that its presence on the B site also removes from observability the ^{7}Li nuclei on adjacent A sites, the tetrahedrally coordinated sites in the spinel structure of lithium titanate. However, a paper describing a new study of the ^{7}Li NMR in this system by Dalton *et al.*[12] is in preparation; it finds that there is no loss of A-site lithium resonance when lithium goes onto the B site.

The μ^-SR experiments[9] have shown that the μ^-O entity is only weakly coupled to the bulk Pauli paramagnetism of a $LiTi_2O_4$ sample; this indicates that the participation of oxygen character in the electron wave functions of the conduction band is weak. Lithium titanate can therefore be viewed as a predominantly d-band metal.

The specific-heat measurements of the normal state[10] find a monotonic reduction of γ, the conduction-electron specific-heat coefficient, with increasing x from 0 to 0.16, followed by a more abrupt decrease for higher x. Somewhat similar behavior is observed also for the variation of T_c with x, although for small x the decrease in T_c is slower than the decrease in γ, while for large x the more abrupt decrease in T_c is to 0 K. The experimental γ value leads to a one-electron density of states $n^0(E_F)$ (having allowed for electron-phonon enhancement effects) of 5.3 states/eV per formula unit, compared to the density obtained from band-structure calculations[4] of 3.3 states/eV per formula unit in the real structure (with the trigonal distortion), and substantially more (5.9 states/eV per formula unit) in the ideal structure. The experimental enhancement over the theoretical prediction indicates some electron-electron correlation.

NMR in titanium metal, hexagonal close packed in structure, reveals[12] an isotropic Knight shift of 0.21% and a rather weak anisotropic component K_{ax} of 0.01%, both dominated by orbital contributions. The s electrons contribute only weakly, via Fermi contact, and core-polarization effects are small. Narath[13] has measured a relaxation time/temperature product (T_1T) in Ti metal of 150 sec K.

Various authors have measured the electron density of states in the substituted lithium titanate system, via photoemission,[14] specific-heat measurements,[10] and magnetic measurements.[15] The photoemission data[14] record a density of states peaked some way away from the Fermi energy and with a value way below that expected from, for example, theoretical calculation.[4,16] These photoemission measurements are not well understood, but appear to indicate both strong electron-phonon and electron-electron interactions in the end member $LiTi_2O_4$. The specific-heat measurement of the density of states has been discussed above.[10] The magnetic measurements[15] predict a density of states in the $x=0$ end member of about 5 states/eV per formula unit, enhanced by a similar amount to the specific-heat value over the band-structure density of states. The impression gained from both susceptibility and specific-heat measurements is that of a Fermi liquid with moderate to strong electron-electron interactions in the x range of 0–0.15, corresponding to a d-band concentration range of $3d^{0.5}$–$3d^{0.3}$. There is little or no evidence, such as depressed magnetism, from these studies of any RVB character.

This paper reports Ti NMR experiments in the temperature range 160–330 K, i.e., $T > T_c$, on a series of lithium titanates $Li_{1+x}Ti_{2-x}O_4$, with x varying from zero to 0.10, in particular, samples $x=0$, 0.01, 0.05, and 0.10, approaching the metal-nonmetal transition. The octahedrally coordinated sites occupied by titanium in the spinel structure have a distorted oxygen environment, and the titanium nucleus is not therefore in an environment of cubic symmetry. This is revealed in the NMR spectra; the effects are monitored as a function of temperature and x. Preliminary measurements of the nuclear spin-lattice relaxation time in the $x=0$ end member and the compatibility of this relaxation with the measured shifts are discussed. The NMR behavior is discussed in the context of structural studies via neutron diffraction on the same samples[7] and magnetic-susceptibility measurements on material prepared in an identical fashion,[17] with reference to the studies listed above on specific-heat[10] and band-structure calculations,[4,16] μ^-SR,[9] NMR in titanium metal,[11] etc. In the next section, we detail our characterization and experimental methods. After that, the experiments on Ti NMR are described and then discussed in the following section.

SAMPLE CHARACTERIZATION AND EXPERIMENTAL METHOD

A full description of the method of preparation of the samples was given recently.[7] The starting materials are Li_2TiO_3, TiO_2, and Ti_2O_3 in the appropriate ratios. Importantly, the authors discuss varying these ratios to take account of the poor stoichiometry of the starting materials. X-ray diffraction of the final materials shows that all the $Li_{1+x}Ti_{2-x}O_4$ are almost single phase, with only tiny quantities of an impurity phase having the disordered rocksalt structure in all samples. They conclude that the samples, as prepared, are of higher quality than in previous studies. The lattice parameter a is consistently higher than previously reported, and the oxygen positional parameter u, measured by neutron diffraction at room temperature, is constant at 0.3876 [with origin at the 8a(Li) site] as x varies. The departure of u from the ideal packing value of 0.375 gives a measure of the amplitude of the trigonal distortion at the titanium sites.

Neutron diffraction[7] further reveals a systematic lithium deficiency on its own tetrahedral site; at $x=0$, only a fraction 0.92 of the tetrahedral sites is occupied by lithium. This appears to be a general feature of these samples; they are deficient in tetrahedral lithium. Interestingly, as x increases, the lithium does not fill up the vacant tetrahedral sites, but goes onto the octahedral sites, substituting for the titanium, with the lithium deficiency on the tetrahedral sites persisting.

Further characterization via ac susceptibility measurements reveals results similar to those of Ueda *et al.*[18] For $x > 0.05$ the measurements[7] indicate a slightly larger "volume fraction" of the superconducting phase in the

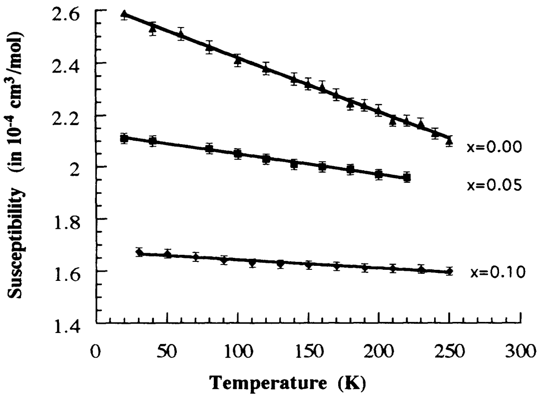

FIG. 1. Susceptibility (after subtraction of a small Curie component) for three samples of $Li_{1+x}Ti_{2-x}$, $x = 0$ (triangles), $x = 0.05$ (squares), and $x = 0.10$ (circles), against temperature. The lines through the data are linear fits.

samples which are the subject of the present work compared to those of Ueda *et al.*[18] This small difference may simply be related to differences of grain size in the two studies.

Superconducting quantum interference device (SQUID) susceptibility measurements indicate that the samples are remarkably free from localized electron spins. The electron-spin susceptibility as a function of temperature for three samples is shown in Fig. 1. (A more detailed report of these susceptibility measurements will appear separately.[17]) A small Curie component was subtracted before plotting Fig. 1. This Curie component, assuming it is of Ti^{3+} character, corresponds to less than 1% of the titanium sites carrying a local moment; 0.25% of Ti sites at $x = 0$ show a Curie moment, while by $x = 0.1$ the number has grown to 0.66%. It is clear that the preparation method has produced samples of $Li_{1+x}Ti_{2-x}O_4$ with far fewer localized spins than have been reported previously (cf., for example, Johnston[19] and Harrison, Edwards, and Goodenough[5,15]). The main difference between the susceptibility results reported in Fig. 1 and those previously published[5,15] lie in the data for the $x = 0$ sample; the data for $x = 0.05$ and 0.10 are almost identical in the two sets. Our $x = 0$ data has a much stronger temperature dependence and has a progressively larger χ as T decreases. We speculate that our preparation method has produced samples with fewer native defects, leading to a situation coming close to the "intrinsic" narrow d-band limit with therefore inherently more temperature dependence in its susceptibility.

The NMR spectra were acquired with a pulsed spin-echo sequence on a Bruker MSL 500 spectrometer using a static probe operating at 11.75 T.

TITANIUM NMR RESULTS

These can be discussed in three separate sections: (i) the variation of the line shape for the $x = 0$ sample in the temperature range 160–330 K, (ii) the effect on the line shape (at room temperature) of the variation of the Li composition over the range $0 < x < 0.10$, and (iii) measurements of the spin-lattice relaxation at both 160 and 293 K.

The line shape at room temperature for $LiTi_2O_4$ is shown in Fig. 2. The reference signal is chosen as the titanium resonance in strontium titanate, $SrTiO_3$, in the

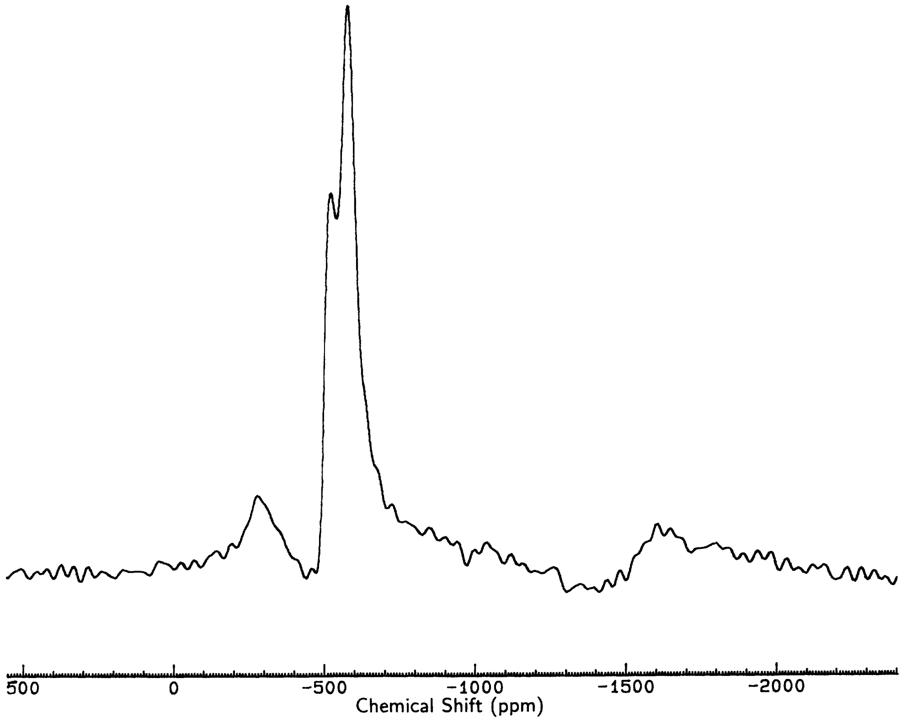

FIG. 2. Typical 293 K spectrum in the $x = 0$ material. In this case, the frequency decreases to the right; the two outer, broader, peaks are for ^{47}Ti, and the just-resolved inner peaks are for ^{49}Ti. All four peaks are singularities from powder spectra and are $\frac{1}{2}$ to $-\frac{1}{2}$ transitions.

solid state; the titanium 49 resonance in this compound has a width of 100 Hz, reflecting the good cubic structure and the absence of any strong magnetic nuclei in this material. The titanium 47 resonance lies about 7.5 kHz away, to lower frequency, and is slightly broader. The split central peak in Fig. 2 is identified as the central ($\frac{1}{2} \leftrightarrow -\frac{1}{2}$) transition of the titanium 49 nucleus, the spectrum of which is broadened and split by a quadrupolar interaction due to a distortion from a cubic symmetry of sufficient magnitude to involve second-order quadrupole effects. The origin of this distortion is the trigonal distortion of oxygen ions in the immediate coordination shell of the titanium, well documented by neutron and x-ray diffraction.[7] The outlying peaks are those of the ^{47}Ti nucleus, similarly split by the quadrupole interaction; here, the splitting is much larger because of the relative quadrupole moments and spin of the ^{47}Ti and ^{49}Ti nuclei (Table I).

TABLE I. Relevant nuclear parameters of ^{47}Ti and ^{49}Ti.

	^{47}Ti	^{49}Ti
Natural abundance (%)	7.28	5.51
Nuclear Spin I	5/2	7/2
Nuclear Quadrupole Moment Q (10^{-24} cm^2)	0.29	0.24
Gyromagnetic ratio $\gamma_n/2\pi$ (MHz/kG)	0.240 00	0.240 05

Since the nuclear gyromagnetic ratios and quadrupole moment ratio for ^{49}Ti and ^{47}Ti are known (Table I),[20] it is straightforward, using the procedure laid down by Jones, Graham, and Barnes,[21] to evaluate the Knight-shift components K_{ax} and K_{iso} (respectively, the axial and isotropic components of the Knight shift) and the quadrupole coupling constant e^2qQ/h. Furthermore, this spectrum has been measured at 160, 220, and 330 K, as well as 293 K, so that the evolution of K_{iso}, K_{ax}, and e^2qQ/h can be followed as a function of temperature.

The method of extracting the requisite parameters from the data involves first the use of Fig. 2 of Jones, Graham, and Barnes[21] [which plots $(\nu_0\Delta\nu)/b$ against $r=a\nu_0^2/b$, where $\Delta\nu$ is the second-order quadrupole splitting of the two resonance peaks for a particular nucleus, $a=K_{\text{ax}}/(1+K_{\text{iso}})$, ν_0 is the Larmor frequency, and b is a measure of the quadrupole interactions and is defined in Jones, Graham, and Barnes[21]]. The spectra, e.g., Fig. 2, are measured to produce a value of $\Delta\nu$ for each of ^{49}Ti and ^{47}Ti. There are constraints that $K_{\text{iso}}^{49}=K_{\text{iso}}^{47}$, $a^{49}=a^{47}$, and $b^{49}=0.291b^{47}$ (from the known quadrupole moments and spin values of the nuclei[20]). Thus an initial working value for r for the titanium 49 nucleus can be deduced with which one can then calculate, using the measured line positions from the spectra for ^{49}Ti, values of K_{iso}, K_{ax}, and e^2qQ/h. These values of K_{iso}, K_{ax}, e^2qQ/h, and r are then used to predict where the ^{47}Ti lines should appear; if these are wrong by any substantial amount, then an iterative loop is entered, whereby r is allowed to vary to improve the fits. Table II shows the measured and predicted ^{47}Ti peak positions as finally revealed by this process.

One rather striking feature of the K_{iso} and K_{ax} plots (Fig. 3) are their similarity; a plot of K_{iso} against K_{ax}, with temperature as the implicit parameter, produces a 45° straight line. In this case, the same temperature variation of either the hyperfine coupling constant or susceptibility drives *both* the isotropic and axial variations of a shift with temperature. A further feature of both plots in Fig. 3 is the possibility that the temperature dependence of both K_{iso} and K_{ax} is disappearing at low temperature.

Figure 4, the variation with temperature of the quadrupole coupling, probably shows the effect of a temperature variation of the distortion described by the parameter u. Note, however, that, over the whole temperature range measured here, the diminution in e^2qQ/h is only about 15% and that any relation between u and e^2qQ/h would almost certainly not be linear; thus, the possibility of following this variation of u with temperature using neutron diffraction may not be as straightforward as one would imagine. Dalton, Green, and Stallick[22] have measured, via neutron diffraction, the temperature variation of u between 6 and 300 K; they find that at 6 K, u takes the value 0.387 61(5), while at 300 K it takes the value 0.387 90(6). In any case, the variation of the quadrupole coupling with temperature may not be directly linked to structural changes, but may be electronic in origin. As has been demonstrated in CuO solids of high-temperature superconductivity materials by Yu *et al.*[23] and Schwarz, Ambrosch-Draxl, and Blaha,[24] the dominant influence on quadrupole effects can be the immediate electronic structure of the ion surrounding the observed nucleus, rather than the configuration of the surrounding ions.

The room-temperature behavior of the spectrum of the titanium resonance as a function of x is striking, with the

TABLE II. Fit between the predicted positions for the ^{47}Ti lines using the K_{iso}, K_{ax}, and quadrupole coupling constants shown in Figs. 3 and 4 and the actual measured positions. The units of the peak positions are ppm with respect to the SrTiO$_3$ reference. ν_H and ν_L refer to the positions of the high- and low-frequency peaks in the spectrum, respectively.

	ν_H		ν_L		
Temperature (K)	Measured	Predicted	Measured	Predicted	r value
330	−65	−67	−1037	−1034	3.00
293	−21	−23	−1297	−1285	2.25
220	+45	+35	−1602	−1624	1.45
160	+65	+43	−1833	−1793	1.20

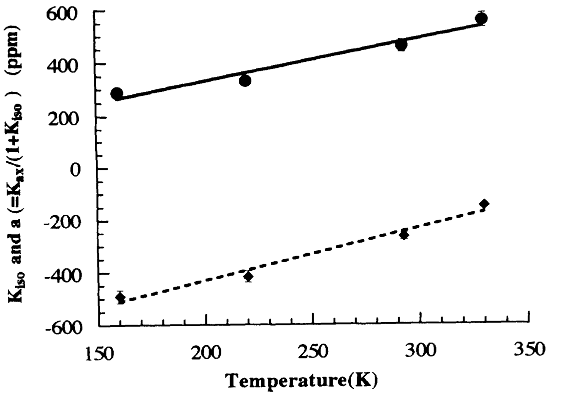

FIG. 3. Plots of K_{iso} and a (approximately the same as K_{ax}) against temperature for the $LiTi_2O_4$ sample. The solid diamonds and dashed line represents K_{iso}; the solid circles and solid line represents a. Both the solid and dashed lines are linear best fits to the data.

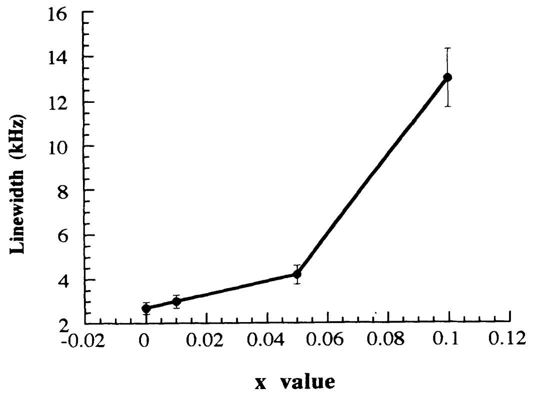

FIG. 5. Plot of the room-temperature NMR linewidth against x for the ^{49}Ti line.

lines rapidly broadening and weakening. Figure 5 details the behavior of the linewidth for the ^{49}Ti nucleus. Above $x = 0$, the broadening eliminates the small splitting of the ^{49}Ti spectrum, yielding a single peak; the position of this peak does not change significantly as x varies, within the error determined by locating the position of peaks as large as those plotted in Fig. 5. For the $x = 0.05$ sample, the behavior of the linewidth and line position as a function of temperature has been followed down to 160 K (Figs. 6 and 7). The line broadens rapidly as the temperature is lowered, and the position becomes more negative.

Attempts were made to measure the nuclear spin-lattice relaxation time for titanium 49 in $LiTi_2O_4$ at the two temperatures 160 and 293 K. The recoveries are very nonexponential, not analyzable in any simple way, and the recovery appears to be similar at the two temperatures. At room temperature there is a very fast relaxation component of about 1 ms of about one-third of the total signal amplitude and a larger component of about 100 ms; at 160 K, the fast component is much slower, about 4 ms, while the longer component is about 50 ms. This sort of non-Korringa behavior is reminiscent of copper relaxation in Y-Ba-Cu-O.[25]

DISCUSSION

The first point to comment on is that, in the $LiTi_2O_4$ sample, only one titanium site is observed in these experiments, having the same quadrupole interaction and Knight-shift characteristics; either all the titanium in the sample has these same characteristics, or only some of the titanium is observed, and the rest is unobservable for some reason, such as a very short T_2 or random variation of the quadrupole coupling. Given the x-ray and other evidence that the $x = 0$ system is definitely monophase, then the conclusion that all the Ti is observed is reasonable. As the spectrum broadens and weakens for $x > 0$, a rough line intensity comparison with the $x = 0$ sample makes it clear that all the Ti is still observed, but that increasingly as x increases and disorder increases with lithium substitution, the quadrupole interaction and Knight shifts start to vary from site to site, producing a broadening of the spectra.

The measured axial and isotropic Knight shifts, referenced with respect to the titanium resonance in strontium titanate, are all small and strongly temperature depen-

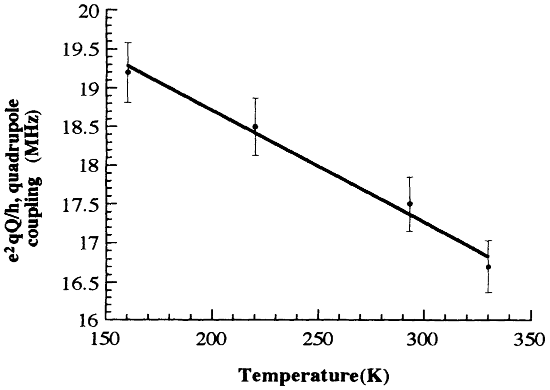

FIG. 4. Quadrupole coupling constant e^2qQ/h for ^{49}Ti is plotted against temperature for the $LiTi_2O_4$ sample. The line through the data is a linear fit.

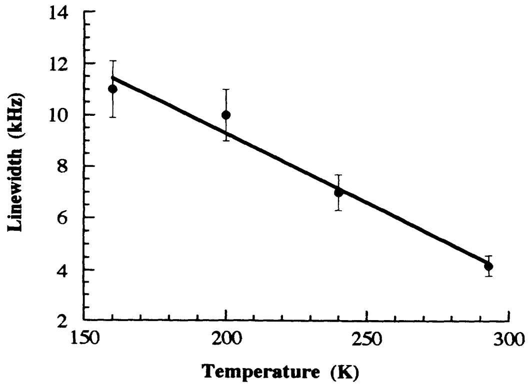

FIG. 6. ^{49}Ti linewidth plotted as a function of temperature for the $Li_{1.05}Ti_{1.95}O_4$ sample. The line is a linear fit.

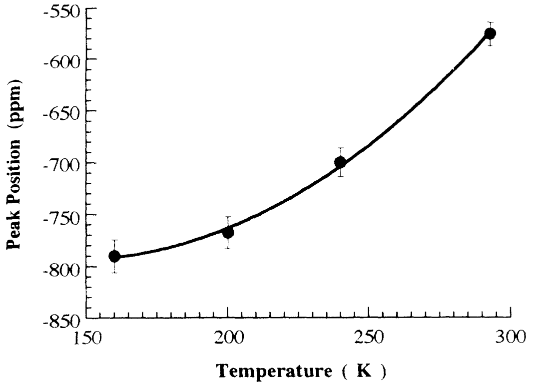

FIG. 7. ^{49}Ti peak position for the $Li_{1.05}Ti_{1.95}O_4$ sample is plotted against temperature. The line through the data is a second-order polynomial fit.

dent, consistent with a narrow d band formed by direct overlap of t_{2g} titanium orbitals.[5,14] The question of whether $SrTiO_3$ is an appropriate reference should perhaps be addressed first before too many conclusions are drawn about shift magnitudes. Hao *et al.*[26] and Traill and Young[27] detail the wide range of shift in titanium compounds in liquids, varying over at least 1000 ppm. For example, in the series $TiCl_4$:$TiBr_4$:TiI_4 the shifts vary from 0 to 483 to 1278 ppm. In the present case, however, the reference compound and the compound being measured both have titanium coordinated by six oxygen ions, and the only differences lie in the degree to which the d band is populated (it is clearly empty for fully stoichiometric $SrTiO_3$) and in the presence of the small trigonal distortion of the oxygen octahedron in $LiTi_2O_4$. The effect of this trigonal distortion on chemical shifts for the central nucleus seems likely to be small. A common reference for high-resolution Ti NMR is $TiCl_4$; relative to strontium titanate, its resonance is shifted by $+840$ ppm. Nonetheless, we feel that strontium titanate is the appropriate reference for our purposes.

As noted earlier, the shift in titanium metal,[11] hexagonal close-packed structure, is $+2100$ ppm and is predominantly orbital in character. The isotropic shifts in the $x=0$ compound (Fig. 3) vary from -500 to -150 ppm, the negative sign indicating a core-polarization mechanism. The dominance of core polarization over orbital effects in the shifts and relaxation of d-band metals is associated with a strong exchange enhancement via electron-electron interactions,[28] and so the change of mechanism between Ti metal and $LiTi_2O_4$ is an indication of the increased importance of electron-electron interactions in $LiTi_2O_4$ originating from the narrower d band in the compound as compared to the metal. A narrow d-band metal and its associated high density of states are also often correlated with strong electron-phonon interactions[29] and, hence, with superconductivity of the BCS type. Figure 3 shows a strongly *increasing* anisotropy as the temperature increases. The similarity in shapes of the plots in Fig. 3 points strongly to a common physical origin for the variation of K_{ax} and K_{iso}. In the $x=0.05$ material (Fig. 7), the same general trend with temperature is observed; bear in mind, however, that this graph plots the peak position, since the isotropic and axial components cannot be disentangled at this concentration. It is probable that the same mechanism is at work in these two samples, $x=0$ and 0.05.

The question arises as to whether these changes in shifts with temperature for the $x=0$ sample are driven by the susceptibility changes (Fig. 1). Figure 8 plots K_{iso} and $a=K_{ax}/(1+K_{iso})$ against the susceptibility changes from 160 K upwards. (Since the Knight-shift data go up to 330 K and the susceptibility data terminate at 250 K, a linear extrapolation of the susceptibility with temperature from 250 to 330 K has been used.) Given the error bars, the fits are reasonable; the slope of the K_{iso} against χ leads to a reasonable value for the hyperfine field at the Ti sites of -55 kG.

Following the analysis of Johnston,[19] the susceptibility of each of the series of lithium titanates can be broken down into the sum of a core contribution, which is in this case close to zero, a Landau contribution from the diamagnetic susceptibility of the conduction electrons, a contribution from the Pauli paramagnetism of the conduction electrons, and an orbital paramagnetic contribution from the conduction electrons. The Landau contribution is negligible.

The two substantial contributions to the susceptibility each produce a corresponding Knight shift; K_s is the spin shift due to the Pauli paramagnetism, and K_{orb} is the orbital shift. Band calculations indicate a negligible s character at the Fermi surface, so that the only spin shift is that due to the d electrons; hence, a core-polarization mechanism is indicated, K_s^d, with a negative value (we neglect dipolar contributions). The temperature dependences observed in the Knight shift (Fig. 3) and in the susceptibility (Fig. 1) may be assumed to be caused by the variation of the d-electron spin susceptibility, following Clogston, Jaccarino, and Yafet.[30]

To push the analysis of the temperature dependences

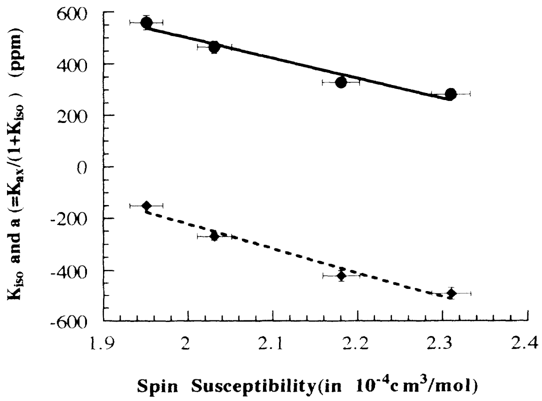

FIG. 8. For the $LiTi_2O_4$ sample, plots of the measured isotropic Knight shift and axial shift parameter a against the susceptibility with temperature as the implicit parameter. Note that the values of the susceptibility at the two highest temperatures have been obtained by a linear extrapolation to higher temperatures of the data in Fig. 1.

of the $x=0$ shifts and susceptibility further, an estimate is needed of the orbital hyperfine field (since no measurements of K_{orb} have yet been made in the superconducting state, where spin contributions to shift and susceptibility vanish). Ebert, Winter, and Voitlander[31] have calculated orbital hyperfine fields in V, Cr, Nb, and Mo, getting values ranging from 812 kG to 1.158 MG. There appears to be a tendency for these hyperfine fields to decrease as the d band empties, so that, for the titanate $3d^{0.5}$ system, a reasonable estimate of the orbital hyperfine field would be 500 kG. Another estimate can be generated from Clogston, Jaccarino, and Yafet,[30]

$$H_{\mathrm{orb}}=2\beta\langle r^{-3}\rangle ,$$

where $\langle r^{-3}\rangle$ may be taken from the tabulated theoretical values for Ti^{3+} in Abragam and Bleaney.[32] After allowing for some expansion of the wave function in the metal, by taking $\langle r^{-3}\rangle$ to be 75% of the tabulated, theoretical, free-ion value, this produces a value of the orbital hyperfine field of about 220 kG. Lacking any other indicators, a value of 300 kG will be assumed for this hyperfine field in $\mathrm{LiTi_2O_4}$. Now the construction of Clogston, Jaccarino, and Yafet[30] is followed and reproduced in Fig. 9. The deduced orbital susceptibility is small $(30\pm5)\times10^{-6}$ emu/mol. The net Knight shift is seen to be composed of a temperature-independent orbital contribution of 1300 ppm and a rather larger, in magnitude, core-polarization term.

Yasui and Shimizu[33] have calculated orbital susceptibilities across the $3d$ transition-metal series and have established that at low filling (and remember $\mathrm{LiTi_2O_4}$ is a $3d^{0.5}$ system) of the $3d$ band the orbital susceptibility is small, fully consistent with the value deduced from the Knight-shift measurements above. Clogston, Jaccarino, and Yafet[30] had made the point earlier that orbital susceptibilities should vary as the product N_oN_u, where N_o/N_u is the number of occupied/unoccupied states in the $3d$ band.

Turning next to the anisotropic component of the Knight shift in the $x=0$ material, the similar temperature dependences of the isotropic and anisotropic components (Fig. 3) confirm that they are driven by the variation of the same susceptibility. The net axial component is positive, composed of a strong positive orbital anisotropy and a weaker core-polarization anisotropy of opposite sign. Orbital and core-polarization hyperfine fields are isotropic, so that the anisotropies observed here must be caused by the susceptibilities; i.e., both the orbital and spin susceptibilities must be anisotropic. In comparison, in hexagonal titanium metal,[11] the anisotropy in the shift is small relative to the isotropic component, and the main contribution comes from the orbital component. On theoretical grounds, band-structure calculations in both lithium titanate[16] and titanium metal would indicate considerably more anisotropy in the former, where the trigonal distortion lowers the energy of one member of the t_{2g} manifold relative to the other two, leaving the wave functions very anisotropic near the Fermi level.

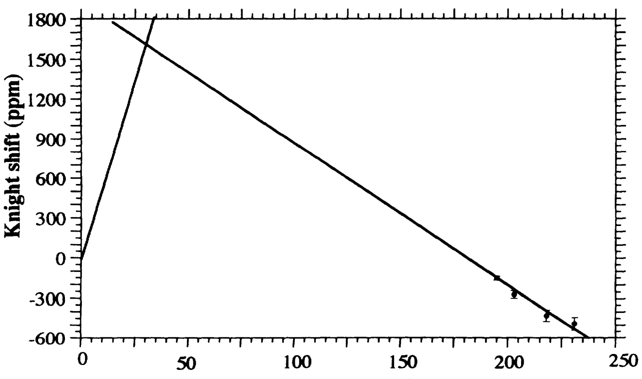

FIG. 9. Construction of Clogston, Jaccarino, and Yafet (Ref. 30), where the Knight shift is plotted against the observed susceptibility and extrapolated back to meet a line drawn from the origin with a slope equal to the orbital hyperfine field.

There has been a quantitative calculation of the spin-lattice relaxation in titanium metal (Asada and Terakura[34]), and Ebert, Abart, and Voitlander[11] show that the paper by Asada and Terakura[34] contains all the requisite parameters for calculating shift values; it would be of value here if similar theoretical calculations could be carried out on the lithium titanate system.

The behavior of the linewidth as a function of temperature for $\mathrm{LiTi_2O_4}$ is consistent with the belief [corroborated by SQUID and electron-spin-resonance (ESR) measurements] that this sample has almost no localized moments. There appears to be little or no variation of the widths of the spectra on variation of the temperature in the $x=0$ sample. The growth in linewidth as the temperature decreases for the $x=0.05$ sample (Fig. 6) could indicate that significant numbers of such moments appear. The susceptibility data above make this unlikely. However, if the anisotropic Knight shift had a similar behavior in this sample to its behavior in the $x=0$ sample (Fig. 3) then the increasing magnitude of the anisotropy as T decreases would cause a broadening of the unresolved pair of lines. The behavior of the linewidth at room temperature as a function of x (Fig. 5) probably reflects the increasing disorder as x increases. There does not appear to be any "wipe-out" effect, as has been observed for the Li resonance,[8] although more recent data[12] appear to contradict the results of Itoh *et al.* The presence of a Li ion on an octahedral site does not appear to eliminate, at room temperature, any extra integrated resonance intensity from the Ti NMR. Lithium substitution for titanium is known to cause major perturbations to the conductivity and superconductivity behavior,[6] indicating strong scattering of electrons at the octahedral lithium sites (Ueda *et al.*[18] note a 1000-fold increase in the normal-state resistivity on increasing x from 0 to 0.12), and it is generally true that doping of metals causes major perturbations in the electronic structure in the immediate vicinity of the dopant.[35,36] The results presented here appear to indicate that the lithium on octahedral sites produces scattering of a type that does not cause quadrupole interactions on adjacent Ti sites large enough to eliminate intensity from the second-order broadened Ti NMR line. Zn substitution in Cu produces[37] quadrupole interactions of 2 MHz, and the NMR frequency of the present lithium titanate experiments is only 28 MHz; if Li substitution generated interactions at near-neighbor Ti sites of 2 MHz, then this would "wipe out" the intensity from the ^{49}Ti line.

At $x=0$, the value of e^2qQ/h decreases monotonically with temperature (Fig. 4), a feature that was initially assumed to be associated with a decrease of the oxygen position parameter u. However, the u variation with temperature is very small.[22] The temperature must drive electronic repopulation among the available bands, and this leads on in turn to a variation in e^2qQ/h and the Knight-shift components.

The relaxation is much too fast for normal Korringa behavior given the measured net shifts of a few hundred ppm. A test for whether the mechanism is magnetic or quadrupolar, by checking which of the two isotopes relaxed the faster, revealed similar rates, thus indicating that the mechanism is indeed magnetic in origin. The absence of local moments in the $x=0$ sample has already been emphasized, so that there seems no chance that paramagnetic impurities can be a significant cause of relaxation. There is always a problem with measuring relaxation times of second-order quadrupolar split spectra[38] from powder samples, which is compounded in this case by the presence of two overlapping spectra, one from ^{49}Ti and the other from ^{47}Ti; further difficulty is caused by the rather weak character of the titanium resonances. Some care was taken by, for example, varying the length of the saturating comb sequences to eliminate sources of uncertainty. It is of interest to consider at this juncture what sort of relaxation rate would be generated by "normal' metallic theory[39] in the light of the metallic shifts measured earlier (Fig. 9). For a core-polarization mechanism via d-spin susceptibility, the relevant Korringa relation between shift and relaxation rate is[28]

$$K^2T_1T=(h/4\pi k_B)(\gamma_e/\gamma_n)^2F^{-1}\ ,$$

where the factor F^{-1} is related to the orbital degeneracy in the d band. This is a factor difficult to estimate in the present context, but its value must lie within the limits of 1 and 5; 2.5 is a reasonable value to take here. For $K\sim 2000$ ppm and a temperature of 200 K, a value of T_1 of about 200 msec emerges. Given the measured values of the longer component of around 100 msec and the possible further contribution from orbital relaxation (for which no Korringa relation holds), the agreement is reasonable. There remains the problem that the relaxation at the lowest temperature appears to be faster than at room temperature. The resolution of this problem will come with more detailed relaxation measurements.

CONCLUSION

A study of the titanium (^{47}Ti and ^{49}Ti) NMR in the normal state of the superconductor $\mathrm{LiTi_2O_4}$ and its lithium-substituted derivatives $\mathrm{Li_{1+x}Ti_{2-x}O_4}$, $0<x<0.1$, has been presented here. Both nuclear magnetic resonance shifts and relaxation rates are studied. In the end member $\mathrm{LiTi_2O_4}$, the second-order quadrupole-split spectra reveal that the temperature variation is such that the anisotropic shift becomes larger while the quadrupole interaction gets smaller as the temperature rises. The variation of the spectra with x reveals that the titanium intensity does not appear to be eliminated from the resonance by lithium substitution. An analysis of the variation with temperature of the shifts reveals that the small observed net isotropic shift is really a juxtaposition of an orbital and a larger core-polarization shift. Taken together, these provide a reasonable explanation of the rather fast spin-lattice relaxation times observed. The susceptibility breaks down into a small orbital contribution 30×10^{-6} emu/mol and a rather larger spin susceptibility which is temperature dependent.

The anisotropic shift is composed of an orbital component and a smaller spin component of similar sizes to the isotropic components. We speculate that the trigonal distortion in the lattice leaves the conduction band at the Fermi surface composed of very anisotropic wave functions.

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[1] D. C. Johnston, H. Prakash, W. H. Zachariasen, and R. Viswanathan, Mater. Res. Bull. **8**, 777 (1973).

[2] P. W. Anderson, Science **235**, 1196 (1987).

[3] Y. Tokura, Y. Taguchi, Y. Okada, Y. Fujishima, T. Arima, T. Kumagai, and Y. Iye, Phys. Rev. Lett. **70**, 2126 (1993).

[4] S. Massidda, J. Yu, and A. J. Freeman, Phys. Rev. B **38**, 11 352 (1988).

[5] M. R. Harrison, P. P. Edwards, and J. B. Goodenough, J. Solid State Chem. **54**, 136 (1984).

[6] P. M. Lambert, M. R. Harrison, D. E. Logan, and P. P. Edwards, in *Disordered Semiconductors*, edited by M. K. Kastner, G. A. Thomas, and S. R. Ovshinsky (Plenum, New York, 1987), p. 135.

[7] M. Dalton, I. Gameson, A. R. Armstrong, and P. P. Edwards, Physica C (to be published).

[8] M. Itoh, Y. Hasegawa, H. Yasuoka, Y. Ueda, and K. Kosuge, Physica C **157**, 65 (1989).

[9] N. Nishida, S. Okuma, H. Miyatake, S. Shiratake, Y. Hidaka, T. Murakami, Y. Ueda, K. Kosuge, S. Kambe, H. Yasuoka, H. Takagi, S. Uchida, K. Nishiyama, K. Nagamine, Y. Kuno, and T. Yamazaki, Hyperfine Interact. **65**, 1027 (1990).

[10] J. M. Heintz, M. Drillon, R. Kuentzler, Y. Dossmann, J. P. Kappler, O. Durmeyer, and F. Gautier, Z. Phys. B **76**, 303 (1989).

[11] H. Ebert, J. Abart, and J. Voitlander, J. Phys. F **16**, 1287 (1986).

[12] M. Dalton, D. P. Tunstall, J. Todd, S. Arumugam, and P. P. Edwards, J. Phys. Condens. Matter (to be published).

[13] A. Narath, Phys. Rev. **162**, 320 (1967).

[14] P. P. Edwards, R. G. Egdell, I. Fragala, J. B. Goodenough, M. R. Harrison, A. F. Orchard, and E. G. Scott, J. Solid State Chem. **54**, 127 (1984).

[15] M. R. Harrison, P. Edwards, and J. B. Goodenough, Philos. Mag. **52**, 679 (1985).

[16] S. Satpathy and R. M. Martin, Phys. Rev. B **36**, 7269 (1987).

[17] M. Dalton and P. P. Edwards (unpublished); M. Dalton, Ph.D. thesis, University of Cambridge, 1993.

[18] Y. Ueda, T. Tanaka, K. Kosuge, M. Ishikawaand, and H. Yasuoka, J. Solid State Chem. **77**, 401 (1988).

[19] D. C. Johnston, J. Low Temp. Phys. **25**, 145 (1976).

[20] T. J. Bastow, J. Phys. Condens. Matter **1**, 4985 (1989).

[21] W. H. Jones, T. P. Graham, and R. G. Barnes, Phys. Rev. **132**, 1898 (1963).

[22] M. Dalton, M. Green, and J. Stallick (unpublished).

[23] J. Yu, A. J. Freeman, R. Podloucky, P. Herzig, and P. Weinberger, Phys. Rev. B **43**, 532 (1991).

[24] K. Schwarz, C. Ambrosch-Draxl, and P. Blaha, Phys. Rev. B **42**, 2051 (1990).

[25] R. E. Walstedt, W. W. Warren, Jr., R. F. Bell, G. F. Brennert, G. P. Espinosa, R. Cava, L. F. Schneemeyer, and J. V. Waszczak, Phys. Rev. B **38**, 9299 (1988).

[26] N. Hao, B. G. Sayer, G. Denes, D. G. Bickley, C. Detellier, and M. J. McGlinchey, J. Magn. Reson. **50**, 50 (1982).

[27] P. T. Traill and C. G. Young, J. Magn. Reson. **90**, 551 (1990).

[28] A. Narath, J. Appl. Phys. **41**, 1122 (1970).

[29] W. L. McMillan, Phys. Rev. **167**, 331 (1968).

[30] A. M. Clogston, V. Jaccarino, and Y. Yafet, Phys. Rev. **134**, A650 (1964).

[31] H. Ebert, H. Winter, and J. Voitlander, J. Phys. F **16**, 1133 (1986).

[32] A. Abragam and B. Bleaney, *Electron Paramagnetic Resonance of Transition Ions* (Clarendon, Oxford, 1970).

[33] M. Yasui and M. Shimizu, J. Phys. F **9**, 1653 (1979).

[34] T. Asada and K. Terakura, J. Phys. F **12**, 1387 (1982).

[35] A. Blandin and J. Friedel, J. Phys. Radium **21**, 689 (1960).

[36] W. Kohn and S. H. Vosko, Phys. Rev. **119**, 912 (1960).

[37] A. G. Redfield, Phys. Rev. **130**, 589 (1963).

[38] E. R. Andrew and D. P. Tunstall, Proc. Phys. Soc. London **78**, 1 (1961).

[39] J. Korringa, Physica **16**, 601 (1950).