Examing the metal-to-insulator transitions in Li$_{1+x}$Ti$_{2-x}$O$_4$ and LiAl$_y$Ti$_{2-y}$O$_4$ with a Quantum Site Percolation model

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We have studied the composition-induced metal-to-insulator transitions (MIT) of cation substituted Lithium Titanate, in the forms Li$_{1+x}$Ti$_{2-x}$O$_4$ and LiAl$_y$Ti$_{2-y}$O$_4$, utilising a quantum site percolation model, and we argue that such a model provides a very reliable representation of the non-interacting electrons in this material if strong correlations are ignored. We then determine whether or not such a model of 3$d^4$ electrons moving on the Ti (corner-sharing tetrahedral) sublattice describes the observed MITs, with the critical concentration defined by the matching of the mobility edge and the chemical potential. Our analysis leads to quantitative predictions that are in disagreement with those measured experimentally. For example, experimentally for the LiAl$_y$Ti$_{2-y}$O$_4$ compound an AI concentration of $y_c \approx 0.33$ produces a metal-to-insulator transition, whereas our analysis of a quantum site percolation model predicts $y_c \approx 0.83$. One hypothesis that is consistent with these results is that since strong correlations are ignored in our quantum site percolation model, which includes the effects of configurational disorder only, such strong electronic correlations are both present and important.

The oxide spinel LiTi$_2$O$_4$ has been the subject of considerable experimental and theoretical study. It was first synthesised and structurally characterised in 1971 by Deschanvres et al. Superconductivity, at 11K, was identified in 1973 by one of the present authors and his collaborators. A comprehensive study of the normal state and superconducting properties of Li$_{1+x}$Ti$_{2-x}$O$_4$ (for $0 \leq x \leq 1/3$) was reported in 1976 and a superconducting transition temperature of 13K was observed. A recent review highlights many of the advances made since then.

There are several reasons to study this system. Firstly, it is interesting to note that superconductivity among spinel systems is very rare; e.g., of the 300 or so known spinels only four of them are superconductors - CuRh$_2$Sc$_4$ ($T_c = 3.49$ K), CuV$_2$S$_4$ ($T_c = 4.45$ K), CuRh$_2$S$_4$ ($T_c = 4.8$ K), and LiTi$_2$O$_4$ ($T_c = 11.3$ K) - and only one of these four is an oxide. So, that oxide, LiTi$_2$O$_4$, has the highest transition temperature of any spinel. Secondly, conduction in this system is believed to take place on the Ti sublattice via the $t_{2g}$ orbitals, as suggested, e.g., by electronic structure calculations and these sites form a corner-sharing tetrahedral lattice(CSTL). Thus, this system represents an example of conduction on a fully frustrated three-dimensional lattice. Also, in this paper we will argue, supported by considerable experimental evidence, that the conduction paths of Li$_{1+x}$Ti$_{2-x}$O$_4$ and LiAl$_y$Ti$_{2-y}$O$_4$ are excellent physical realizations of quantum site percolation.

Furthermore, and central to the motivation for our work, these same electronic structure calculations point out that this is a narrow band electronic system, with the bandwidth of the $t_{2g}$ bands of the order of 2-3 eV, thus suggesting that perhaps strong electronic correlations are present and important. Indeed, others have reached similar conclusions; notably, the phase diagram of Alex Müller summarising a view of how the increased strength of electronic correlations in transition metal oxides leads to higher and higher superconducting temperatures, includes the Lithium Titanate system. Although the original experiments and analysis suggested a weak-coupling BCS-like s-wave superconductor, it was later suggested that off stoichiometry this material is in fact an “anomalous” superconductor (although this claim is not without criticism). We also mention that photoemission studies of Edwards, et al are interpreted in terms of strong correlations, and magnetic susceptibility and specific heat data are interpreted in terms of a density of states that is moderately to strongly enhanced (see Ref. for a discussion of these and other experiments). Taken together, these experimental results form a reasonably strong case for the presence of electronic correlations that are important to the physics of these materials.

Lastly, we mention the recent discovery of the first $d$-electron heavy fermion compound, LiV$_2$O$_4$. This system also assumes the spinel structure, but so far no superconductivity has been observed. The active transition metal ion in LiV$_2$O$_4$ has a formal valence of $d^{<5}$, whereas for LiTi$_2$O$_4$ one considers $d^{0.5}$ ions. Thus, LiTi$_2$O$_4$ is a lower electronic density system than LiV$_2$O$_4$, and an understanding of its behaviour would seem to be a prerequisite to a full understanding of the Vanadate material. For example, why does LiTi$_2$O$_4$ superconductor, with a relatively high $T_c$, while LiV$_2$O$_4$ does not superconduct at all?

In attempt to gain more understanding of the LiTi$_2$O$_4$ system, and, in particular, to try and un-
understand whether or not strong electronic correlations are present, we have examined the density driven metal-to-insulator transition (MIT) of the related Li$_{1+x}$Ti$_{2-x}$O$_4$ and LiAl$_y$Ti$_{2-y}$O$_4$ compounds; for $x_{MIT} \sim 0.12$ and $y_{MIT} \sim 1/3$, transitions of similar to a non-metallic state (which we refer to as insulating) are encountered. To be specific, we use a one electron approach to study this transition employing a quantum site percolation model. Our work may be viewed as addressing the question of whether or not the MIT undergone by this system is driven by disorder only, similar to an Anderson-like MIT. We find that the answer is no, and thus this work provides indirect theoretical support for the proposal that strong electronic correlations are important in a description of the complicated transitions undergone in the LiTi$_2$O$_4$ class of materials.

To fully explain our model we note the following: (i) Electronic structure calculations show that the bands arising from the Ti 3d orbitals are separated from the O 2p band by about 2.4 eV; thus, the electronic valence state may be represented as Li$^{+1}(Ti^{+3.5})_2(O^{-2})_4$, and we ignore the oxygen sites and focus on only the Ti sites. The crystal octahedral field around Ti cations splits the Ti 3d bands into two separate and nonoverlapping $t_{2g}$ and $e_{g}$ bands, with the $e_{g}$ bands split off above the $t_{2g}$ bands. Thus, formally this is a very low filling system — 1/12th filling of each of the (approximately) degenerate $t_{2g}$ bands. Although we have generalized our work to include all three $t_{2g}$ bands, here we will present results for a one-band model of the Ti sublattice, and thus the stoichiometric compound is represented by a 1/4-filled band. (ii) Crystallographic refinements of the excess Li system Li$_{1+x}$Ti$_{2-x}$O$_4$ and the doped Al system LiAl$_y$Ti$_{2-y}$O$_4$ have consistently demonstrated that both the excess Li and doped Al ions enter substitutionally onto the Ti sublattice (octahedral sites of the spinel structure). Assuming that the Li/Al ions that are substituted into the corner-sharing tetrahedral lattice are fully ionised, these sites would block any conduction electrons from hopping onto such sites; e.g., a simple argument supporting this follows from noting that the Li$^+$ ions will be at least doubly negatively charged relative to the occupied Ti$^{3+}$ and unoccupied Ti$^{4+}$ sites that would exist in the absence of substituting Li, and thus electrons will avoid these sites in favour of the Ti sites. We shall assume that these Li-substituting sites are removed from the sites available to the conduction electrons, which implies that this system represents an excellent physical realization of site percolation.

Using such a model the simplest approach to characterising the MIT would be to then associate the transition with the critical concentration at which the classical percolation threshold is reached. For corner-sharing tetrahedral lattices, we have completed a large scale Hoshen-Kopelman search, and have determined that this concentration corresponds to a probability of finding an occupied site at the transition of $p_c \sim 0.39 \pm 0.01$. Noting that the relationship between the probability $p$ of site being occupied by a Ti ion (in the stoichiometric Ti sublattice), and the excess Li concentration $x$, is given by $x = 2(1 - p)$, with an identical $y = 2(1 - p)$ relation for Al added to the Ti sublattice, in contrast to previous statements, this $p_c$ corresponds to a critical excess Li, or added Al, of $x_c = y_c = 2(1 - p_c) \sim 1.2$; that is Li$_{2.2}$Ti$_{0.8}$O$_4$ or LiAl$_{1.2}$Ti$_{0.8}$O$_4$. These very high levels of doping are well beyond the observed $x_{MIT} \sim 0.15$ or $y_{MIT} \sim 0.33$ concentrations at which the MIT occurs. In fact, such a system would require large positive Ti valencies well beyond anything seen in nature! Thus, the physics of these MITs is more complicated than simply the loss of an infinite maximally connected cluster at $p_c$.

We now consider a more accurate model for this system, a so-called quantum site percolation model, which includes the dynamics of the electrons hopping on the conducting, disordered sublattice of Ti sites. To be specific, the near-neighbour tight-binding Hamiltonian for LiTi$_2$O$_4$ is

$$\hat{H} = \sum_i \varepsilon_i c_i^\dagger c_i - t \sum_{<ij>} (c_i^\dagger c_j + h.c.) \tag{1}$$

where $i$ labels the sites of the (ordered) Ti sublattice, $c_i^\dagger$ ($c_i$) is the creation (annihilation) operator of an electron at site $i$, $\sum_{<ij>}$ represents the sum over all nearest neighbour sites of a corner-sharing tetrahedral lattice, and $t$ is the near-neighbour hopping energy. To produce our model of quantum site percolation for the doped systems, the on-site energy $\varepsilon_i$ is determined by the probability of occupation, denoted by $p$, of a site being either a Ti ion, or a Li or Al dopant ion:

$$P(\varepsilon_i) = p\delta(\varepsilon_i - \varepsilon_{Ti}) + (1 - p)\delta(\varepsilon_i - \varepsilon_X) \tag{2}$$

where $\varepsilon_{Ti}$ ($\varepsilon_X$) is the on-site energy when an electron occupies a Ti ($X = Li$ or Al) site. In order to enforce that itinerant electrons move only on Ti sites we set $\varepsilon_{Ti} = 0$ and $\varepsilon_X \to \infty$, and this limit connects this system with a quantum site percolation Hamiltonian. Such considerations lead to the introduction of the quantum percolation threshold usually denoted by $p_q$. To be specific, $p_q$ is reached when all single-electron energy eigenstates of the above tight-binding Hamiltonian are localized. That means that $p_q$ is always larger than $p_c$ since the presence of extended states necessarily requires an infinite maximally connected cluster. Further, the evaluation of this quantity is warranted since $p_q > p_c$ implies that the theoretical predictions of $x_c$ and $y_c$ given above would be reduced by quantum percolation.

Our evaluation of $p_q$ for the corner-sharing tetrahedral lattice proceeds as follows. We have considered various realizations of site percolated lattices for several system sizes for a range of dopant concentrations; to be specific, we consider lattices of size two, four, six, and eight cubed conventional unit cells (noting that there are 16 Ti sites in the ordered lattice per conventional unit cell), and then for each $p$ we examine 100, 50, 20 and 10 realizations consistent with this $p$, for two, four, six, and
eight cubed lattices, respectively. For each realization we first apply the Hoshen-Kopelman algorithm to identify the maximally connected cluster. Then, we diagonalize the one-electron Hamiltonian describing the electron dynamics on this cluster. Then, to determine the localized vs. delocalized nature of the single-electron wave functions for the maximally connected cluster, we have used the scaling of the relative localization length as a function of system size, as described by Sigeti et al. This localization length, for a particular eigenstate, is defined by

$$\lambda = \sum_{ij} |\psi_i|^2 |\psi_j|^2 d(i,j)$$  \hfill (3)$$

where $|\psi_i|^2$ is the probability amplitude for this eigenstate at site $i$, and $d(i,j)$ is the Euclidean distance between lattice sites $i$ and $j$. Then, the relative localization length is just the ratio of this quantity to that for a state having a uniform probability amplitude throughout the entire maximally connected cluster (we denote the latter by $\lambda_0$) — this ratio thus provides a useful measure of the effective size, or localization, of a particular eigenstate relative to a Bloch state on the same maximally connected cluster. The utility of this quantity (and we will describe its use for another problem below) is that if the quantity decreases as the system size is increased, then that eigenstate corresponds to one that is spatially localized; the opposite behaviour is expected for delocalized states. We have used this quantity as a means of identifying $p_q$.

As a test of this method, we note that for three-dimensional lattices, reliable estimates exist only for the simple cubic lattice, and these were obtained with a variety of different methods — e.g., see the discussion in Ref.\textsuperscript{12} A value of $p_q = 0.44 \pm 0.02$ was identified\textsuperscript{12} and we have found that our method reproduces this number.

Using this method we find a value of $p_q$ for corner-sharing tetrahedral lattices (with near-neighbour hopping only) of $p_q = 0.52 \pm 0.02$, and if we then associate this quantity with the concentration at which the MIT occurs in doped LiTi$_2$O$_4$, one finds $x_c = y_c = 2(1 - p_q) = 0.96$, which correspond to Li$_{1.96}$Ti$_{1.04}$O$_4$ and LiAl$_{0.96}$Ti$_{1.04}$O$_4$. Again, these concentrations are much higher than the experimentally measured values.

The reason for both of these failures is clear and has been suggested before\textsuperscript{15} — as the concentration of doped cations is increased, the density of available 3$d$ electrons is decreased. In fact, for $x_{BI} \equiv 0.33$ and $y_{BI} \equiv 1.0$ these materials become insulators simply because the bands of all allowed states are empty (we refer to such a state as a Band Insulator (BI)). So, if a one-electron description is going to correctly reproduce the MIT, we must account for the changing of the electronic density with cation dopant concentration. (This notwithstanding, we needed to determine what values of $x_c$ and $y_c$ were predicted by $p_q$ in case they were less than either $x_{BI}$, or $y_{BI}$, respectively. Clearly, they are not.)

Also, since the above arguments point to Ti occupation probabilities well above the quantum percolation threshold, we might as well attempt to use the concept of quantum percolation. (e) The so-called quantum percolation threshold is reached when all electronic states have a localized character (regardless of the location of the chemical potential).
threshold, one is guaranteed to find a maximally connected cluster, and (possibly) several isolated clusters. By definition, all electronic states associated with an isolated cluster are localized, while for the maximally connected cluster both extended and localized states will be found. Similar to Anderson localization of disordered systems, we expect that the eigenstates of the maximally connected cluster and all isolated clusters, have been evaluated since the latter contribute to the location of the chemical potential.

The mobility edge has been estimated using the above-mentioned scaling method and Fig. 3 depicts the application of this method to identify the location of mobility edge for the specific doping concentration of $x = 0.7$. To be concrete, one can estimate that for this dopant concentration the mobility edge, in units of the hopping energy $t$, is $-4.0 \pm 0.15$.

We have combined all of our data in Fig. 4 which shows the chemical potential and mobility edge that we would estimate for both the excess Li and doped Al systems. For reference we have included the values of the band minimum for all dopings. Note that the Fermi level of the excess Li system crosses the mobility edge at roughly $x_c \approx 0.324$, whereas for the doped Al system this crossing occurs at $y_c \approx 0.83$. Clearly, these numbers are much larger than the experimental values ($x_{MIT} \approx 0.15$ and $y_{MIT} \approx 0.33$). Thus, we have studied a system that should be very well represented, in a one-electron theory, by a quantum site percolation model, have determined the concentrations at which the Fermi levels cross the mobility edge, and find these values to be a factors of 2 and greater than 3 larger than the experimental results. So, we believe that this shows that a one-electron model, that ignores electronic correlations, cannot explain the observed MITs.

Example density of states curves, and the locations of the chemical potentials, are shown in Fig. 2 for different doping concentrations, averaged over systems with 8-cubed conventional unit cells (the largest studied). Note that the full spectrum of eigenvalues, of both the maximally connected cluster and all isolated clusters,
FIG. 4: This plot displays the final numerical results of our study, and leads to the identification of predicted concentrations at which the MITs occur. These data are the chemical potentials ($\mu_F$) and mobility edge as a function of doping for both $\text{Li}_{1+x}\text{Ti}_{2-x}\text{O}_4$ and $\text{LiAl}_y\text{Ti}_{2-y}\text{O}_4$; for reference we have also plotted the minimum of the band of electronic states. The crossing of the chemical potential and mobility edge (denoted by open black circles) would indicate the position of disorder-only induced metal-to-insulator transition, and these values are labelled $x_c$ and $y_c$.

Concluding, our results show that disorder-only models of the MITs undergone by these systems substantially overestimate the critical concentrations of doped cations. To be specific, for $\text{Li}_{1+x}\text{Ti}_{2-x}\text{O}_4$ our numerical result for $x_c$ is a little more than double the experimental value, and for $\text{LiAl}_y\text{Ti}_{2-y}\text{O}_4$ our numerical result is an even larger multiple. (We note that we have not eliminated the possibility that polaronic effects give rise to this transition, although no experimental work points to their existence.) Thus, indirectly, this study supports the hypothesis that strong electronic correlations are important for the MIT, and, possibly, also for the $T_c \sim 13K$ superconducting transition undergone by $\text{LiTi}_2\text{O}_4$.

This past year sample preparation advances have allowed for the growth of large stoichiometric $\text{LiTi}_2\text{O}_4$ single crystals, and a remarkably sharp superconducting transition ($\delta T_c \sim 0.1 \text{K}$) has been observed. We hope that these new samples stimulate further experimental research in this interesting class of materials.

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1. A. Deschanvres, B. Raveau, and Z. Sekkal, Mater. Res. Bull. 6, 699 (1971).
2. D. C. Johnston, H. Prakash, W. H. Zachariasen, and R. Viswanathan, Mater. Res. Bull. 8, 777 (1973).
3. D. C. Johnston, J. Low Temp. Phys. 25, 145 (1976).
4. R. W. McCallum, D. C. Johnston, C. A. Luengo, and M. B. Maple, J. Low Temp. Phys. 25, 177 (1976).
5. E. G. Moshopoulou, J. Am. Ceram. Soc. 82, 3317 (1999).
6. S. Satpathy and R. M. Martin, Phys. Rev. B 36, 7269 (1987).
7. S. Massidda, J. Yu, and A. J. Freeman, Phys. Rev. B 38, 11352 (1988).
8. S. Kirkpatrick and T. P. Eggarter, Phys. Rev. B 6, 3598 (1972).
9. Y. Shapir, A. Aharony, and A. B. Harris, Phys. Rev. Lett. 49, 486 (1982).
10. K. A. Müller, in Proceedings of the 10th Anniversary HTS Workshop on Physics, Materials, and Applications, edited by B. Batlogg et al. (World Scientific, 1996), p. 1.
11. J. M. Heintz et al., Cond. Mat.: Z. Phys. B 76, 303 (1989).
12. J. F. Annett, Physica C 318, 1 (1999).
13. P. P. Edwards et al., J. Sol. St. Chem. 54, 127 (1984).
14. M. R. Harrison, P. P. Edwards, and J. B. Goodenough, J. Sol. St. Chem. 54, 136 (1984).
15. D. P. Dunstall et al., Phys. Rev. B 50, 16451 (1994).
16. S. Kondo, D. C. Johnston, et al., Phys. Rev. Lett. 78, 3729 (1997).
17. M. R. Harrison, P. P. Edwards, and J. B. Goodenough, Phil. Mag. B 52, 679 (1985).
18. P. M. Lambert et al., in Disordered Semiconductors, edited by M. A. Kastner et al. (Plenum Press, 1987), pp. 135–149.
19. P. M. Lambert, P. P. Edwards, and M. R. Harrison, J. Sol. St. Chem. 89, 345 (1990).
20. M. R. Harrison, Ph.D. thesis, Oxford University (1981).
21. P. M. Lambert, Ph.D. thesis, Cornell University (1986).
22. J. Hoshen and R. Kopelman, Phys. Rev. B 14, 3438 (1976).
23. D. E. Sigeti et al., Phys. Rev. B 44, 614 (1991).
24. C. M. Soukoulis, Q. Li, and G. S. Grest, Phys. Rev. B 45, 7724 (1992).
25. P. W. Anderson, Phys. Rev. 109, 1492 (1958).
26. C. Chen et al., J. Crystal Growth 250, 139 (2003).