The role of strong electronic correlations
in the metal-to-insulator transition in disordered LiAl$_y$Ti$_{2-y}$O$_4$

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Abstract

The compound LiAl$_y$Ti$_{2-y}$O$_4$ undergoes a metal-to-insulator transition for $y_c \sim 0.33$. It is known that disorder alone is insufficient to explain this transition; e.g., a quantum site percolation model predicts $y_c \sim 0.8$. We have included (Hubbard) electronic interactions into a model of this compound, using a real-space Hartree-Fock approach that achieves self consistency at every site, and have found that for a Hubbard energy equal to 1.5 times the non-interacting bandwidth one obtains $y_c \sim 0.3$. Further, with increasing Hubbard energy we find an Altshuler-Aronov suppression of the density of states, $\delta N(\epsilon) \sim \sqrt{|\epsilon - \epsilon_F|}$, that reduces the density of states at the Fermi energy to zero at the critical Hubbard interaction. Using this ratio of correlation to hopping energy one is led to a prediction of the near-neighbour superexchange ($J/t \sim 1/3$) which is similar to that for the cuprate superconductors.
The range of interesting phenomena of transition metal systems includes the anomalous normal state and high-temperature superconductivity of the quasi-2d cuprates, as well as the colossal magnetoresistance of the manganites and related systems. The ubiquitous physics believed to be responsible for these novel behaviours is strong electron-electron interactions, a consequence of which is the inapplicability of Landau’s theory of fermi liquids.

One interesting class of related materials are the spinels. There are over 300 transition metal spinels, out of which only four are superconducting. Further, of these four only one is an oxide, and that oxide, LiTi$_2$O$_4$, has the highest superconducting transition temperature, $T_c$: CuRh$_2$Se$_4$ ($T_c = 3.49$ 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).

LiTi$_2$O$_4$ is a 1/4-filled $d^{0.5}$ system in which the electronic conduction occurs via direct $d-d$ hopping on the Ti sites, owing to the orientation of the low-lying $t_{2g}$ orbitals. The Ti sublattice corresponds to a corner-sharing tetrahedral lattice (CSTL), which is a fully frustrated three dimensional (3d) structure. It has been suggested by Bednorz and Müller that this system is moderately correlated electronic system, and that the superconductivity may be driven by the electronic interactions amongst the $d$ electrons. However, other reasons behind our interest in this system include: (i) A metal-to-insulator transition generated by both disorder and a reduced electronic density caused by chemically substituting Li, Al or Cr for Ti – this transition is the focus of this paper. (ii) If strong electronic correlations are present then the magnetic properties of this material could be interesting, corresponding to a 1/4-filled fully frustrated lattice. (iii) The isostructural $d^{1.5}$ LiV$_2$O$_4$ is believed to be a $d$-electron heavy fermion compound, and understanding the simpler (1/2 an itinerant electron per site in LiTi$_2$O$_4$ vs. the 1.5 electron per site (1 local moment plus 1/2 an itinerant electron per site)) LiV$_2$O$_4$ would be highly beneficial.

In the tight-binding approximation, a reasonable Hamiltonian from which to begin a study of disordered LiAl$_y$Ti$_{2-y}$O$_4$ is given by

$$H = \sum_{i,\sigma} \varepsilon_i n_{i,\sigma} - t \sum_{\langle ij \rangle,\sigma} (c_{i\sigma}^\dagger c_{j\sigma} + h.c.) + U \sum_i n_{i\uparrow} n_{i\downarrow}$$

where $i$ denotes a Ti site on a CSTL, and $c_{i\sigma}$ the annihilation operator for an electron at site $i$ with spin $\sigma$, and $n_{i,\sigma} = c_{i\sigma}^\dagger c_{i\sigma}$. (For reference below, note that the noninteracting bandwidth is $8t$.)

As mentioned above, there are a variety of different chemical dopings that lead to a
metal-to-insulator transition (MIT), but here we focus on LiAl$_y$Ti$_{2-y}$O$_4$, which undergoes a MIT for $y \sim 0.33$. In this system the Al$^{3+}$ ions substitute onto the Ti sublattice, and thus in a first approximation the on-site energies are chosen at random according to the distribution function

$$P(\varepsilon_i) = (1 - \frac{y}{2}) \delta(\varepsilon_i - \varepsilon_{\text{Ti}}) + \frac{y}{2} \delta(\varepsilon_i - \varepsilon_{\text{Al}}).$$

Then, in the expected limit of $\varepsilon_{\text{Al}} - \varepsilon_{\text{Ti}} \gg 8t$, if one ignores the presence of electron-electron interactions one sees that this system is an excellent representation of quantum site percolation (QSP). Previously, three of us have analyzed such a QSP model for noninteracting electrons ($U = 0$) on a CSTL, and (numerically) exactly solved the disordered electron problem (energies and eigenfunctions) for various large lattice sizes, thus determining the Fermi energy, $E_f(y)$, and mobility edge, $E_c(y)$, as a function of Al doping concentrations.

We found that at $y = y_c \sim 0.8$ the Fermi energy and mobility edges crosses, and in such a disordered, noninteracting model this would correspond to the predicted MIT. The large disagreement between the experimental value of $y_c \sim 0.33$ and our prediction ($y_c \sim 0.8$) highlights that important physics has been omitted in such an analysis.

Indirectly, the above result supports the conjecture that strong electronic correlations are present and play an important role in the physics of LiTi$_2$O$_4$. Of course, to provide substance to this idea we need to examine the full disordered and interacting electron problem, and to this end we have analyzed the behaviour of such a disordered-Hubbard Hamiltonian, viz. we have studied Eq. (1) with the Ti conduction path limited by the full QSP model mentioned above, now including the Hubbard interaction term. This is a relatively complicated model which contains the interplay between electronic correlations and disorder produced by quantum-site-percolation, and in the following we describe our results of a comprehensive examination of this problem in a real-space self-consistent Hartree-Fock approximation. Recent results for a disordered Hubbard model on a two-dimensional square lattice have lead to the interesting prediction of a novel metallic phase; here we use the same formalism, but now for a 3d CSTL.

In such a real-space self-consistent Hartree-Fock formulation one replaces the Hubbard interaction term as follows:

$$U \sum_i n_{i\uparrow} n_{i\downarrow} \simeq U \sum_i \left( \langle n_{i\uparrow} \rangle \langle n_{i\downarrow} \rangle + \langle n_{i\downarrow} \rangle \langle n_{i\uparrow} \rangle - \langle n_{i\uparrow} \rangle \langle n_{i\downarrow} \rangle \right),$$

(3)
where the primed summation indicates that only Ti sites (from both the maximally connected, and possibly isolated clusters) are included. Then the interacting Hamiltonian is simplified to

$$H_{\text{eff}} = -t \sum_{\langle ij \rangle, \sigma} \langle i \uparrow| c_i^\dagger c_j \sigma \rangle \langle j \downarrow| c_j^\dagger c_i \sigma \rangle - U \sum_i \langle n_i \uparrow \rangle \langle n_i \downarrow \rangle$$

where

$$\langle n_i \sigma \rangle = \sum_{\alpha \sigma} \langle \epsilon_{\sigma} \leq \epsilon_F | \psi_{\alpha \sigma} i \rangle |^2 , \quad (5)$$

and

$$H_{\text{eff}} | \psi_{\alpha \sigma} \rangle = \epsilon_{\alpha \sigma} | \psi_{\alpha \sigma} \rangle \quad (6)$$

Here, $|i\rangle$ is a single orbital Wannier function at site $i$ from the Ti sublattice, $|\psi_{\alpha \sigma} \rangle$ are the energy eigenstates of the effective Hamiltonian, $\langle n_i \sigma \rangle$ is the average density of electrons with spin $\sigma$ at site $i$, and $\epsilon_F$ is the Fermi energy \[13\].

In order to find self-consistent solutions for the above Hamiltonian, we start with the noninteracting but disordered tight-binding model on a CSTL, and obtain the expectation values of the density of electrons on each site using Eq. (5) – this is the distribution of the density of electrons for a non-interacting QSP disordered system for a specific filling factor of the LiAl$_y$Ti$_{2-y}$O$_4$ system. We then iterate to convergence at every site as $U$ is increased from zero. Note that in the iteration sequence we have added a small random fluctuation in the on-site densities for each site and each spin, to allow for the system to proceed to a non-paramagnetic state if it so chooses.

This procedure has been applied to CSTL, with random QSP determined by $y$, for system sizes of 5488, 8192, 11664 and 16000 lattice sites with periodic boundary conditions. For each system size the spectrum of eigenvalues and the distribution of the electron density throughout the lattice were calculated for each realization of disorder, for doping concentrations of $y = 0.2, 0.3, 0.4, 0.6, 0.7$, and $0.75$, and for Hubbard interaction strengths of $U/t = 2, 4, 6, 8, 10$, and $12$. Then, these calculations were repeated for different complexions of disorder for each set of values of $y$ and $U/t$.

Density of states results are shown in Fig. 11 for a doping concentration of $y = 0.3$ and for three different Hubbard interactions of $U/t = 4, 8, 12$, for systems with 16000 lattice sites.
FIG. 1: Density of states for a single realization of disorder in the Hubbard+QSP model for the LiAl$_{y}$Ti$_{2-y}$O$_4$ system with $y = 0.3$ and $U/t = 4, 8, 12$ for a system with 16000 lattice sites. The suppression that is associated with the Altshuler-Aronov square-root singularity is evident, as is the complete suppression (zero density of states at the Fermi level) at the critical ($U_c/t, y_c$).

The interesting feature in these plots is the suppression of the density of states at the Fermi level with increasing $U$. That is, as a function of increasing Hubbard energy, we find that a progressively larger change of the density of states consistent with the predictions of the theory of Altshuler and Aronov [14], namely a square-root suppression near the Fermi level of the form $\delta N(\epsilon) \sim \sqrt{|\epsilon - \epsilon_F|}$. In fact, we find a complete suppression that first appears at the critical Hubbard interaction (see below) associated with the metal-to-insulator transition. These and our previous density of states data [10] are consistent with the hypothesis that only in an interacting system should one find such effects. Lastly, we note that recent experimental investigations [15] of other transition metal oxides have seen precisely this form of the density of states, on the metallic side, as the metal-to-insulator transition is approached.

In order to characterize the metallic or insulating behaviour of such systems, we examined the eigenstates of a small energy bin ($\Delta E/t = 0.1$) located symmetrically about the Fermi energy, and calculated the average inverse participation ratio (IPR), averaged over a sufficient number of realizations to obtain converged data. A collection of our results for the
IPRs vs. the inverse of the system size is shown in Fig. 2. From the linear fits of the IPRs vs. the inverse of the system size, the values of the IPRs in the thermodynamic limit can be extracted. We also determined the 98% confidence level (2× the standard deviation) error bars of the intercepts. As is well known, if the extrapolated value of the IPR has a finite intercept then the eigenstates corresponding to that specific system, in that energy range, are localized, and in the subsequent discussion we use the criterion that the intercept must be at least twice the standard deviation above zero before we classify (with a 98% confidence level) that those energy eigenstates are of a localized nature. For example, for $y = 0.3$ for $U/t = 2$ to 10 the states near the Fermi level are extended, whereas for $U/t = 12$ these same states are localized. Consequently, as a function of increasing Hubbard interaction we identify the MIT as occurring at $U_c/t \sim 11 - 12$ for $y = 0.3$.

Repeating this sequence of calculations for the above-mentioned $y$ and $U/t$ we identified
a phase diagram of the \((T = 0)\) metal-to-insulator transition of this system with respect to disorder and interaction, and our results are depicted in Fig. 3. We immediately see that if strong electronic correlations are indeed an important aspect of the physics associated with this transition, that is for a \(y_{\text{exp}} \sim 0.33\), we require a \(U/t \sim 11 - 12\). Noting that for the noninteracting electrons on this lattice one has a bandwidth of \(8t\), this implies that LiTi₂O₄ is a moderately correlated three-dimensional electronic system. This is consistent with conclusions drawn, albeit indirectly, from recent low-temperature specific heat measurements[16] in this material.

In fact, this value is not far from experimental estimates of \(U/t\) for the \(t_{2g}\) \(d\) orbitals of related Ti-based transition metal oxides. That is, the estimate for the Hubbard on-site repulsion for the \(t_{2g}\) orbitals of Ti atoms in the perovskite LaTiO₃ is \(U_{t_{2g}} \sim 3.1eV\) [17]. Resonant soft-x-ray emission spectroscopy on perovskite-type Ti compound \(La_xSr_{1-x}TiO_3\) provides an estimate of \(U_{d-d} \sim 4.0 - 4.4eV\) [18, 19], with the most recent estimate being \(U/t \sim 4.0eV(2003)\) [19]. Now compare these estimates to our predicted value of \(U\) for the \(LiAl_yTi_{2-y}O_4\) system: taking into account the estimate for the transfer integral of \(t \sim 0.33eV\) for the \(t_{2g}\) band in this system based on the LDA calculations[4, 5], using \(U_c/t = 11 - 12\) (for \(y = 0.3\)) our estimate of \(U\) corresponds to 3.7-4.0 eV. Clearly, our estimate is not dissimilar to the experimentally observed values for these related Ti-based oxides.

We note that this energy leads to a provocative comparison between the near-neighbour superexchange \((J)\) between moments in this system vs. those in the high-temperature superconducting cuprates. That is, using \(J = 4t^2/U\) for this one-band system we find that in \(LiTi_2O_4\) \(J/t \approx 1/3\), which is similar to the estimates for the cuprates. So, this similarity also lends support to the hypothesis of Bednorz and Müller[6] of the potential relation of the pairing in this system to the cuprates.

As further corroboration of our phase diagram results, and to gain a better understanding of how the transition is connected to the electronic and magnetic properties of this system, we have examined the (spin-resolved) charge and magnetic densities as a function of disorder and Hubbard energy. Our results for the variation of the number of electrons per site are effectively independent of spin, and are shown in Fig. 4. We see that for \(y = 0.3\), for \(U/t = 0\) to 8, essentially no change takes place. However, as \(U/t\) is increased from 8 to 10 to 12 this quantity undergoes substantial change. That is, when the Hubbard energy approaches the
critical value (for this $y$) due to the proliferation of localized states arising from the suppression of the density of states at the Fermi level, one finds a far more inhomogeneous system. Also, our numerical results for the local magnetizations correspond to the appearance of (short-ranged) antiferromagnetic correlations at the metal-to-insulator transition. That is, as $U/t$ is increased towards $U_c/t(y)$ this distribution gradually changes from a rather narrow peak at zero (paramagnetism), to a distribution dominated by two broad peaks at $\pm m_0$, with $m_0 \sim 0.4$, corresponding to a locally antiferromagnetic arrangement but with many sites having largely paramagnetic character.

Summarizing, we have used a real-space self-consistent Hartree-Fock formulation to examine the metal-to-insulator transition in disordered LiAl$_y$Ti$_{2-y}$O$_4$; this work (i) treats the disorder exactly (that is, diagonalizing the full Hamiltonian matrix for any particular complexion of disorder), and (ii) involves solving for the self-consistent solutions at every site. We have found that to obtain agreement with the experimentally observed concentration of Al impurities at which the metal-to-insulator transition occurs, a Hubbard energy somewhat larger than the noninteracting bandwidth is required, consistent with recent experiments on this system [16], and that the resulting density of states as the transition is approached is similar to that found in experiments on related materials [15].

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FIG. 4: The distribution of single-site charge densities for $y = 0.3$ as a function of increasing Hubbard energy $U/t$. One sees a profound change in the homogeneity of the charge density as $U/t$ approaches the critical value at which the metal-to-insulator transition occurs.

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