Role of Magnetic Moments in the Metal-to-Insulator Transition in LiAl$_y$Ti$_{2-y}$O$_4$

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Abstract. While the high-$T_c$ cuprate problem remains an active field of research, several parallel studies in potentially related physical systems have been undertaken. For example, LiTi$_2$O$_4$, known to have a superconducting $T_c$ of about 13K, has been suggested to have a strong relation to the cuprates. Our studies are addressing the key question: Are strong electronic correlations found in LiTi$_2$O$_4$? To answer this we have focussed on a study of the metal-to-insulator transition that LiAl$_y$Ti$_{2-y}$O$_4$ is found to undergo for $y \sim 0.3$, and have modelled this material using a quantum-site percolation model that includes electronic correlations through an on-site repulsive Hubbard interaction. We find that in such a model this transition is reproduced through the appearance of an Altshuler-Aronov-like suppression of the density of states at the Fermi level, called by some a pseudogap, when an intermediate-strength Hubbard interaction is introduced. Here we focus on results displaying the essential role that magnetic moments that develop on the Ti sites seem to play in producing this transition, physics absent from the original Altshuler-Aronov analysis.

1. Introduction

The oxide spinel LiTi$_2$O$_4$ has been the subject of considerable experimental and theoretical study. It was first synthesized and structurally characterized in 1971 by Deschanvres et al [1]. Superconductivity was identified in 1973 by one of the present authors and his collaborators [2], and 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 — a superconducting transition temperature of around 13 K was observed [3, 4]. A recent review [5] highlights many of the advances made since then.

There are several reasons to study this system. First, it is interesting to note that superconductivity among spinel systems is very rare [5]; e.g., of the 300 or so known spinels, only four of them are superconductors - 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) - and only one of these four is an oxide. So, that oxide, LiTi$_2$O$_4$, has the highest transition temperature of any spinel. Second, 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 [6, 7], 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. Further, and central to the motivation for our work, these same electronic structure calculations [6, 7] 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 [8], summarizing 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 [4], it was later suggested [9] that off stoichiometry this material is in fact an “anomalous” superconductor. We also mention that photoemission studies of Edwards, et al. [10] are interpreted in terms of strong correlations, and magnetic susceptibility [11] and specific heat data [9] are interpreted in terms of a density of states that is moderately to strongly enhanced (see Ref. [12] 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.

In attempt to gain more understanding of the LiTi$_2$O$_4$ system, and, in particular, to try and understand whether or not strong electronic correlations are present, we have examined the metal-to-insulator transition (MIT) of the related LiAl$_y$Ti$_2-y$O$_4$ compound: for $y_{MIT} \sim 1/3$ a transition [3, 13, 9, 14, 15] to a non-metallic state (which we refer to as insulating) is encountered. Our previous work [16, 17] has shown that models based on disorder alone are unable to explain this transition, but that if one includes an on-site repulsive interaction (the so-called Hubbard interaction energy) one generates a large suppression of the density of states at the fermi level, and that the resulting system is non-metallic [18].

Our previously published result [18] was found from a real-space self-consistent Hartree-Fock (HF) treatment of a quantum-site percolation model that included a Hubbard interaction. The disorder is treated exactly, via the exact diagonalization of effective-one-electron Hamiltonians, whereas the interactions are treated approximately (that is, within HF). In this communication we show that (i) the result is not particular to a corner-sharing tetrahedral lattice - here we present results of our study of a simple cubic lattice; (ii) the result does not require quantum site percolation, and indeed the result applies to other models of disorder - in our present study we utilized a model with a box distribution of on-site energies, where the “strength” of the disorder is half that of the kinetic energy (unlike a quantum site percolation model in which the on-site energies of one atomic species are taken to be infinite); and most importantly (iii) we show that if one employs a restricted HF treatment in which the HF wave functions are forced to be paramagnetic then no suppression of the density of states at the fermi level occurs, and therefore no metal-to-insulator transition is found. Local moment formation is essential if, at least within HF, one is to generate such a transition.

2. Theoretical Formalism and Results
Theoretically, the simplest model that hopefully represents some of the key physics of such systems is the so-called Anderson-Hubbard Hamiltonian. The Anderson model [19] is given by

$$\hat{H}_A = \sum_{i,\sigma} V_i \hat{n}_{i,\sigma} - t \sum_{(i,j),\sigma} \left( \hat{c}_{i,\sigma}^\dagger \hat{c}_{j,\sigma} + \text{h.c.} \right)$$ (1)

where $i, j = 1 \ldots N$ denote the sites of the lattice, $(i, j)$ implies that $i$ and $j$ are near neighbours, $\hat{c}_{i,\sigma}$ ($\hat{n}_{i,\sigma}$) is the destruction (number) operator for an electron at site $i$ with spin $\sigma$, and the hopping energy is denoted by $t$. The on-site energy at site $i$ is given by $V_i$, and one may employ differing models of disorder. For example, (i) a quantum site percolation model corresponds...
$V_i = 0$ for one set of (conducting) sites and $V_i = \infty$ for all other sites; (ii) an AB binary alloy model, where $V_i$ is set equal to $W/2$ (for an $A$ site) or $-W/2$ (for a $B$ site); (iii) a box distribution of on-site energies in which all site energies in the range $-W/2$ to $+W/2$ are equally likely. The electron interactions that are included are represented by the Hubbard term [20], given by

$$\hat{H}_H = U \sum_i \hat{n}_{i,\uparrow} \hat{n}_{i,\downarrow}$$  \hspace{1cm} (2)

The Anderson-Hubbard model is formed from the sum of $\hat{H}_A$ and $\hat{H}_H$.

The HF decoupling scheme is well known, but for completeness we summarize the final results. The HF technique can be thought of as an approach in which one ignores terms in the interaction Hamiltonian, viz. the Hubbard Hamiltonian of Eq. (2), that are proportional to fluctuations about mean values squared. That is, one approximates the local Hubbard interaction as being replaced by (here we ignore the possibility of local superconducting pairing correlations)

$$\langle \hat{n}_{i,\uparrow} \hat{n}_{i,\downarrow} \rangle = (\bar{n}_{i,\uparrow} + \delta \hat{n}_{i,\uparrow})(\bar{n}_{i,\downarrow} + \delta \hat{n}_{i,\downarrow}) - (h^+_{i} + \delta h^+_{i})(h^-_{i} + \delta h^-_{i})$$  \hspace{1cm} (3)

and the effective local fields $h^\pm_{i}$ are given by $h^+_{i} \equiv \langle \hat{S}^+_{i} \rangle$ and $h^-_{i} \equiv \langle \hat{S}^-_{i} \rangle$. Then, one must find self consistently the local spin-resolved charge densities and local fields that minimize the variational estimate of the ground-state energy.

In our previous work we restricted the moments to be along the quantization axis, meaning that for the solutions in Ref. [18] the effective fields $h^\pm_{i} = 0$. Here we show results from two different starting points. First, we relax this condition on the effective fields and allow for them to be real, which means that the moments can now point in any direction in the $xz$ plane. Second, we have completely suppressed the moments by solving the paramagnetic HF problem, meaning that $\bar{n}_{i,\uparrow} = \bar{n}_{i,\downarrow}$ and the effective fields $h^\pm_{i} = 0$. For both of these studies, instead of the fully frustrated corner-sharing tetrahedral lattice [18] we have studied a three-dimensional simply cubic lattice (which is bipartite and therefore not frustrated).

Our results are shown in figure 1 (see caption for energy parameter, etc.), from which a strong suppression of the density of states at the fermi level is found for non-paramagnetic HF, but that no suppression is found for paramagnetic HF. Also, we find that the specific lattice does not matter - we find a suppression of the density of states for both a corner-sharing tetrahedral lattice [18] and here for a simple cubic lattice. The model of disorder does not matter - we find a suppression with either a quantum site percolation model [18] or for a uniform box distribution of disorder of weak to intermediate strengths (other disorder strengths produce similar results). Further, the spins found in the non-paramagnetic HF ground state turn out to be strongly non-collinear, so the restriction of collinear spins used in [18] is also not essential. Local moment formation is essential if, at least within HF, one is to generate a metal-to-insulator transition in the Anderson-Hubbard model (at least away from 1/2 filling, for which the Mott gap can introduce other physics).

As discussed previously, the theory of Altshuler and Aronov [21] predicts such a “pseudogap” due to the combined effects of correlations and disorder. However, this theory makes no assumption concerning the development of the local magnetic moments and its relation to the appearance of the density of states suppression. However, our real-space self-consistent Hartree-Fock results make clear that the appearance of such spin moments may be related to such physics [22], and therefore to the metal-to-insulator transition.

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The lattice size is $18^3$, the energy scales are $U/t = 11.5$ and $W/t = 6$, corresponding to intermediate coupling and weak disorder. The electronic density is $1/4$ filling, similar to those studied by us elsewhere [18]. The solid black curve is the density of states found from a PM real-space self-consistent Hartree-Fock approximation that enforces $n_i^\uparrow = n_i^\downarrow$ and zero effective fields, whereas the red dashed curve is found from an unrestricted HF approximation that produces both non-zero local spin moments and non-collinear spins.

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