Doped Mott insulator as the origin of heavy Fermion behavior in LiV$_2$O$_4$

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We investigate the electronic structure of LiV$_2$O$_4$, for which heavy fermion behavior has been observed in various experiments, by the combination of the local density approximation and dynamical mean field theory. To obtain results at zero temperature, we employ the projective quantum Monte Carlo method as an impurity solver. Our results show that the strongly correlated $a_{1g}$ band is a lightly doped Mott insulator which - at low temperatures- shows a sharp (heavy) quasiparticle peak just above the Fermi level, which is consistent with recent photoemission experiment by Shimoyama et al. [Phys. Rev. Lett. 96 026403 (2006)].

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The discovery of heavy fermion (HF) behavior in the 3d material LiV$_2$O$_4$ [1] was a big surprise since this phenomenon was previously a hallmark of certain f electron compounds. But below a characteristic temperature $T_K \sim 28$ K, the linear specific heat coefficient ($\gamma$) [1], the magnetic susceptibility [1], the Gr"uneisen parameter [2], and the quadratic resistivity coefficient [3] are also for LiV$_2$O$_4$ extraordinarily large, similar to f electron HF compounds and much larger than in other transition metal oxides. From $\gamma \sim 420$ mJ/molK$^2$, an effective mass enhancement of $m^*/m \sim 25$ was inferred [4]. Neutron scattering [3], nuclear magnetic resonance [5] and electron spin resonance [7], as well as muon spin relaxation experiments [8] indicate the existence of local magnetic moments, which is consistent with a Curie-Weiss susceptibility [1] in the temperature range 50 to 1000 K. Down to the lowest temperatures measured LiV$_2$O$_4$ remains a cubic spinel and no long-range magnetic, spin glass, or superconducting order was observed. More recently, also a sharp Kondo peak of width 10 meV was observed in photoemission experiments [3] just 4 meV above the Fermi energy $E_F$, with a strong temperature dependence similar to that of other HF compounds. This finding is supported by the measurement of the magnetic curves at $T = 1.3$ K [10] which also suggests the existence of a sharp peak slightly above $E_F$.

The explanation of the HF behavior in LiV$_2$O$_4$ has been a challenge since its discovery. Local density approximation (LDA) calculations [11, 12] show a twofold-degenerate and 2 eV-wide $e_g^0$ and a nondegenerate $a_{1g}$ band of width 1 eV across the Fermi energy, filled altogether with 1.5 electrons per V ion. This LDA bandstructure led one of the present authors (VIA) to the proposal [11, 12] that the $a_{1g}$ electrons play the role of the localized f electrons in conventional HF compounds and the $e_g^0$ electrons that of the itinerant valence electrons. On the other hand, the importance of geometrical frustration originating in the spined structure has been stressed by various authors [14, 15, 16, 17, 18, 12, 20, 21, 22], all suggesting different explanations for the mass enhancement of LiV$_2$O$_4$. Naturally the geometrical frustration suppresses any kind of long range order, so that local spin or orbital fluctuations should be dominant as suggested in Ref. [20, 21].

In this situation, we might expect dynamical mean field theory (DMFT) [23] to be good approximation for studying the electronic correlations in this material. Realistic LDA+DMFT calculations for LiV$_2$O$_4$ have been carried out before [23], but neglected the $a_{1g} e_g^0$ hybridization, which should be the driving force for the HF behavior in the Kondo scenario [11] and were furthermore restricted to temperatures $T > 750$ K, far above $T_K$. Not surprisingly, a quasiparticle resonance was not found and the competition between antiferromagnetic direct exchange from the $a_{1g} a_{1g}$ hybridization, ferromagnetic double exchange from the $e_g^0 e_g^0$ hybridization, and the Kondo effect from the (neglected) $a_{1g} e_g^0$ hybridization left this LDA+DMFT study [23] inconclusive. Since that time the more sophisticated projection onto Wannier functions has been developed [24] which properly takes the orbital off-diagonal hybridization into account. Also the problem that conventional quantum Monte Carlo (QMC) simulations [27] of the DMFT impurity problem were restricted to rather high temperatures because the numerical effort is proportional to $1/T^3$ has been overcome by the projective QMC (PQMC) method [28, 29, 30] for $T = 0$.

With these improvements, we reinvestigate LiV$_2$O$_4$ by LDA+DMFT(PQMC) and solve the puzzle why this material shows HF behavior with a sharp Kondo peak above the Fermi level.

**Method.** The unit cell of LiV$_2$O$_4$ contains four V atoms and each V atom has three $t_{2g}$ orbitals, which are split into the $a_{1g}$ orbital and two degenerate $e_g^0$ orbitals due to the trigonal splitting. First, we do a LDA calculation for LiV$_2$O$_4$ using the linearized muffin tin orbital
basis set \[31\]. From this we further construct an effective 12 by 12 Hamiltonian by the projection onto Wannier functions \[26\]. Since the \(e_g^\pi\) orbitals are degenerate, it is possible to derive a 2-orbital model with an 8 by 8 Hamiltonian by taking only one of two \(e_g^\pi\) orbitals into account. This drastically decreases the computational efforts of the LDA+DMFT calculation and hence allows for more accurate data. As we will see \textit{a posteriori}, the restriction to one \(e_g^\pi\) orbital will be justified by the fact that the \(e_g^\pi\) orbitals play a rather passive role and the physics is determined by the \(a_{1g}\) band. The comparison of the band dispersion of this simplified 8-band model with total LDA band structure of LiV\(_2\)O\(_4\) in Fig. 1 shows that the 2-orbital simplification captures the essential features of the real compound’s band structure. It also gives the densities of states (DOS) close to that previously reported by LDA, see Fig. 5 in \[25\].

Second, we supplement this 2-orbital Hamiltonian by local intra-(\(U\)) and inter-orbital (\(U'\)) Coulomb repulsions as well as by Hund’s exchange (\(J\)), and solve the constructed many-body model by DMFT. It should be noted that we explicitly consider the off-diagonal elements between \(e_g^\pi\) and \(a_{1g}\) in contrast to all previous calculations \[22\], where only the initial LDA \(a_{1g}^s e_g^\pi\) hybridization is reflected indirectly in the DOS. This \(a_{1g}^s e_g^\pi\) hybridization is essential for the Kondo effect with localized \(a_{1g}\) and itinerant \(e_g^\pi\) electrons \[11\]. As for the self-energy, we only consider the diagonal element, so that the effective DMFT impurity model becomes a two-orbital problem. We also assume that the Hund coupling is of Ising type since simulating the SU(2) symmetric Hund coupling is difficult in QMC. The application of new, more sophisticated algorithms to this end, such as \[32\], remains an important challenge for the future.

Besides conventional QMC, we employed the PQMC method in the present LDA+DMFT calculation, basically following Ref. \[22\] for calculating ground state expectation values. With an imaginary time discretization \(\Delta\tau = 0.267 eV^{-1}\), we take \(\mathcal{E} = 20\) time slices for measurement and \(\mathcal{P} = 65\) time slices before and thereafter for projection. For the remaining imaginary time to \(\beta = \infty\), we use the non-interacting Hamiltonian with a shifted one-particle potential so that we have \(n = 1\) electrons/site for the \(a_{1g}\) orbitals and \(n = 0.25\) for the \(e_g^\pi\) orbitals. This shift warranties (approximately) the same large-\(\tau\) asymptotic behavior as the interacting Hamiltonian. We performed \(\sim 3 \times 10^8\) QMC sweeps and used the maximum entropy method for calculating the spectral function \(A(\omega)\) and the Fourier transformation of the Green function from imaginary time to frequencies, i.e., from \(G(\tau)\) to \(G(i\omega)\).

\textbf{Results.} Let us start with the results of conventional QMC at finite \(T\). In Fig. 2, we plot the spectral function \(A(\omega)\), using Coulomb interaction parameters which are typical for 3\(d\) orbitals, i.e., \(U = 3.6, U' = 2.4,\) and \(J = 0.6\) eV. The qualitative feature of the result for \(\beta = 1/T = 10 eV^{-1}\) corresponding to \(T \approx 1200\) K is similar to that of the previous LDA+DMFT calculation \[25\]. But for \(\beta = 40 eV^{-1}\) (\(T \approx 300\) K) we note the emergence of a small structure in the \(a_{1g}\) band just above \(E_F\), which is absent for \(T \approx 1200\) K. At the same time, we see no noteworthy temperature dependence for the \(e_g^\pi\) band, especially around \(E_F\) (see the inset). As far as the finite-\(T\) QMC is concerned, it is not clear whether the small structure in the \(a_{1g}\) band becomes a sharp quasiparticle peak at lower temperatures.

To clarify this point, let us now turn to the PQMC
results at $T = 0$, see Fig. 3. Indeed we can see in the PQMC spectrum that the small structure just above $E_F$ at $T \approx 300$ K becomes a sharp peak, which is consistent with the experiment [8], i.e., a peak 4 meV above $E_F$ whose width is 10 meV. This $a_{1g}$ band is lightly doped, containing $n = 0.98$ electrons/site. Unfortunately, the exact determination of the renormalization factor ($Z$) from $A(\omega)$ or the self energy is difficult because of the smallness of the structure and fluctuations from iteration to iteration in the DMFT cycle. However, the peak itself is stable as is the behavior of $G(\tau)$, plotted in Fig. 4. The latter shows a very slow decay for large $\tau$ in PQMC which necessitates the existence of a sharp peak at small positive energies in the $a_{1g}$ band. In contrast, for $T \approx 300$ K, $G(\tau)$ vanishes exponentially, see Fig. 4 (a).

**Discussion.** Let us now turn to the physical origin of the sharp peak in the $a_{1g}$ band. One possible scenario which was originally proposed in Ref. [11] is the Kondo effect caused by the hybridization between $a_{1g}$ and $e_g^\pi$ orbitals on neighboring sites (note that the on-site hybridization is absent). However, it is not trivial whether the associated (antiferromagnetic) Kondo coupling is strong enough to survive a Hund’s exchange coupling as large as $J = 0.6$.

To single out the effect of the $a_{1g}$$e_g^\pi$ hybridization, we perform an auxiliary LDA+DMFT calculation. To this end, we first obtain the $a_{1g}$ and $e_g^\pi$ LDA DOS from the effective 2-orbital Hamiltonian and then do DMFT calculations with these DOSes without any hybridization. We plot the resulting $G(\tau)$ and $A(\omega)$ of the $a_{1g}$ band in Fig. 5. Clearly, the sharp peak just above $E_F$ survives switching off the $a_{1g}$$e_g^\pi$ hybridization. Hence, we can conclude that the Kondo scenario due to the hybridization with $e_g^\pi$ orbitals [11] cannot be the microscopic origin for the peak in the $a_{1g}$ band. Actually, besides contributing to the doping of the $a_{1g}$ band, the $e_g^\pi$ electrons do not play a pronounced role and are only weakly correlated. Their self energy (not shown) is almost constant down to very low frequencies $\sim 0.01$ eV. The constant (Im$\Sigma \sim -0.14$ eV) can be explained by non-interacting electrons scattering at disordered spins which is an appropriate description of the $a_{1g}$ electrons except for the lowest energies.

Hence, let us turn to the $a_{1g}$ band itself which is not exactly half-filled, but lightly doped with $n \sim 0.98$ electrons/site. This suggests that the $a_{1g}$ band is a lightly hole-doped Mott insulator with a very strongly renormalized quasiparticle because of the nearness to the doping-controlled Mott-Hubbard transition. We can compare our results with those of Ref. [33] for the single-band Hubbard model on the hypercubic lattice. At $n = 0.97$ and very low temperature, these results show a sharp peak just above $E_F$ [33], very similar to our LDA+DMFT calculations. An important question for this scenario of a doped Mott insulator is whether the strong renormalizations can survive the presence of short-range correlations beyond DMFT. In this respect, the correlator projection method indicates that $Z$ does not vanish for

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**FIG. 3:** (Color online) Same as Fig. 2 but now at $T = 0$ (PQMC), compared to $\beta = 40$ eV$^{-1}$ corresponding to $T \approx 300$ K. In agreement with experiment, we can see a sharp peak slightly above $E_F$ (set to zero) in the $a_{1g}$ band.

**FIG. 4:** (Color online) Green function for the $a_{1g}$ (a) and $e_g^\pi$ (b) orbitals obtained by LDA+DMFT(PQMC) as a function of $\tau$, compared with the result for $\beta = 40$ eV$^{-1}$ ($T \approx 300$ K). In the inset, we magnify the region $\tau > 1$. 

**FIG. 5:** Clearly, the sharp peak just above $E_F$ survives switching off the $a_{1g}$$e_g^\pi$ hybridization. Hence, we can conclude that the Kondo scenario due to the hybridization with $e_g^\pi$ orbitals [11] cannot be the microscopic origin for the peak in the $a_{1g}$ band. Actually, besides contributing to the doping of the $a_{1g}$ band, the $e_g^\pi$ electrons do not play a pronounced role and are only weakly correlated. Their self energy (not shown) is almost constant down to very low frequencies $\sim 0.01$ eV. The constant (Im$\Sigma \sim -0.14$ eV) can be explained by non-interacting electrons scattering at disordered spins which is an appropriate description of the $a_{1g}$ electrons except for the lowest energies.
the filling-control Mott-Hubbard transition in the two-dimensional Hubbard model [34], and also the dynamical vertex approximations [35] shows a strong damping of the quasiparticle peak in the vicinity of the Mott-Hubbard transition due to antiferromagnetic fluctuations beyond-DMFT. However, we believe that such effects are less relevant for LiV$_2$O$_4$ because of the frustrated three-dimensional lattice and because there is no indication that the system is close to a magnetic phase transition.

In conclusion, realistic LDA+DMFT calculations for LiV$_2$O$_4$ show a sharp peak for $T \to 0$ in agreement with photoemission experiments and large renormalizations of the effective mass. The physical origin of this peak is the lightly doping of the $a_{1g}$ band which is hence metallic but very close to a Mott-Hubbard transition. The HF physics is not caused by the hybridization between $a_{1g}$ and itinerant $e_g^\sigma$ orbitals. Instead the $a_{1g}$ orbitals play both roles simultaneously, whereas the $e_g^\sigma$ orbitals are rather passive and not strongly correlated.

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