On the origin of heavy quasiparticles in LiV$_2$O$_4$

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The low-temperature properties of the metal LiV$_2$O$_4$ show many of the characteristic features of heavy-fermion systems like CeAl$_3$ or CeRu$_2$Si$_2$. The coefficient $\gamma$ of the low-temperature specific heat $C = \gamma T$ is large, i.e., $\gamma = 0.35 - 0.42 J/molK^2$, depending on samples and $C(T)$ shows a broad maximum around 16K. The large $\gamma$ value implies a high density of fermionic low-energy excitations. In fact, when $C(T)$ is integrated up to 60K it is found that the associated entropy is close to $2R\ln(2)$ where $R$ is the gas constant. This suggests that there is roughly one excitation per V ion in the system when it is heated up to that temperature, a finding inconceivable for a conventional, partially filled conduction band of d-electrons. In fact, the $\gamma$ value obtained from ab initio band structure calculations turns out to be too small by a factor of 25. In accordance with the observed large $\gamma$ value it is found that also the spin susceptibility $\chi_{sp}(T)$ is similarly enhanced. It is nearly $T$ independent below $T \approx 30K$ with a shallow broad maximum around 16K and a sample dependent increase below 5K. The Sommerfeld-Wilson ratio $\chi_{SW} = \pi^2 k_B^2 \chi_{sp}/(3\mu_B^2\gamma)$ is 1.7 with considerable error bars because of the remaining low temperature variation of $\chi_{sp}(T)$. A ratio of that size shows that the enhancements in $\gamma$ and $\chi_{sp}$ near each other as expected for a metal with an enhanced density of states $N^*(0)$ at the Fermi energy. Remember that $\gamma \approx N^*(0)$ and $\chi_{sp} \approx N^*(0)$ in that case. No (anti)ferromagnetic order was found above 0.02K and no evidence for spin-glass behavior. There are also no indications of charge ordering, i.e., all V sites are equivalent. The low-temperature resistivity is $\rho(T) = \rho_0 + AT^2$ with a large coefficient $A = 2\mu\Omega cm/K^2$ like in other heavy-fermion systems. LiV$_2$O$_4$ is therefore a rare case of a system with heavy quasiparticle excitations which do not involve f electrons.

The physical origin of the low-energy scale associated with the characteristic heavy-fermion excitations has remained unclear. Presently we know of a few physical mechanisms resulting in heavy quasiparticles which all seem inapplicable here.

One well known source is the Kondo effect. It applies to heavy-fermion systems like CeAl$_3$ and requires ions with quasi-localized f electrons of nearly integer number. In fact $\gamma$ is the larger the closer the $f$-count $n_f$ is to an integer, e.g., to $n_f = 1$ in the case of Ce ions. But in LiV$_2$O$_4$ the valency of the V ions is +3.5 and therefore the Kondo effect is excluded here. A second mechanism is realized in Nd$_2$-Ce$_x$CuO$_4$ ($x \approx 0.1 - 0.2$) and is essentially based on the Zeeman effect. It applies to systems with strongly correlated conduction electrons which couple weakly to ions with localized spins, i.e., Nd ions in the above case. This situation can be also excluded for LiV$_2$O$_4$. The same holds true for heavy fermions appearing very close to a quantum critical point, a model which has been suggested for YMn$_2$. There remains the case of heavy quasiparticles caused by charge ordering like in Yb$_4$As$_3$. Here the characteristic feature is the formation of well separated spin $\frac{3}{2}$ Heisenberg chains in a three-dimensional lattice due to charge order. This route seems promising except that there is no change ordering in LiV$_2$O$_4$. In that material all V sites remain equivalent down to the lowest temperatures. Nevertheless, it is this example which leads us to suggest the physical model discussed in the following.

The aim of this communication is to discuss a new scenario for the origin of a low-energy scale. It uses the fact that LiV$_2$O$_4$ has a cubic spinel structure down to the lowest temperatures measured, i.e., the system seemingly does not charge order. But it has obviously strong short-ranged electron correlations. The spinel structure enables us to account for them in a particular way which suggests directly a plausible explanation of the large number of fermionic low-energy excitations as evidenced by the large $\gamma$ coefficient.

In the spinel structure the V ions form corner-sharing tetrahedra. Their sublattice can be viewed as a fcc lat-
tice with every second site removed. A \( V \) ion has six nearest neighbors of its kind and the \( V \) ions are the centers of slightly distorted edge sharing octahedra of oxygen ions. All \( V \) ions are crystallographically equivalent. Spinel structures or pyrochlore lattices give rise to frustrated antiferromagnetic interactions. Resulting forms of a spin-liquid ground-state have been frequently discussed see, e.g., [4–10].

Band structure calculations employing the LDA+\( U \) computational method show that the Fermi energy is placed in vanadium \( t_{2g} \) bands which are well separated from the oxygen \( p \)-bands. The average \( d \)-electron number per \( V \) ion is 1.5. For those electrons we assume the following simplified model Hamiltonian to apply

\[
H = \sum_{(ij), \nu \sigma} t_{\nu}(a_{\nu \sigma}^+(i)a_{\nu \sigma}(j) + h.c.)
+ U \sum_{i, \nu} n_{\nu \uparrow}(i)n_{\nu \downarrow}(i)
+ V_0 \sum_{(ij)} n(i)n(j)
+ J_H \sum_i \mathbf{s}_1(i)\mathbf{s}_2(i)
+ \sum_{(ij)} J_{ij} \mathbf{s}(i)\mathbf{s}(j). \tag{1}
\]

The \( a_{\nu \sigma}^+(i) (a_{\nu \sigma}(i)) \) create (destroy) a \( d \)-electron in orbital \( \nu \) with spin \( \sigma \) at site \( i \). For simplicity we shall use two \( d \)-orbitals only, one pointing along the octahedron axis and the other pointing towards the four oxygen ions within the plane. The first term describes the kinetic energy and only transitions between neighboring sites \( (ij) \) are taken into account. The second and third term account for the on-site Coulomb repulsion of \( d \)-electrons in the same and in different orbitals. Here \( n_{\nu}(i) = \sum_{\sigma} a_{\nu \sigma}^+(i)a_{\nu \sigma}(i) \)
is the number operator. The fourth term describes the Coulomb repulsion of electrons situated on neighboring sites, the fifth term is due to Hund’s rule coupling and the last terms results from superexchange via the oxygen sites. The total spins \( \mathbf{S}_{(ij)} \) of the neighboring sites \( i \) and \( j \) depend on the number of \( d \) electrons at those sites. For a \( d^1 \) configuration \( S = \frac{1}{2} \) while for a \( d^2 \) site \( S = 0 \) or 1 etc. We assume that \( U \) and \( V_0 \) are much larger than the \( t_{\nu} \) while \( J_{ij} \) is expected to be of similar size. A large value of \( U \) implies that only \( d^1 \) and \( d^2 \) configurations need consideration. Moreover, a large value of \( V_0 \) requires that on each tetrahedron two sites are in a \( d^3 \) \( (V^{4+}) \) and two are in a \( d^2 (V^{3+}) \) configurations (tetrahedron rule). This has been first pointed out by Verwey [12] and was discussed in detail by Anderson [10]. Note, that because of an average \( d^{1.5} \) occupancy \( d^2 = d^3 \) and \( d^1 - d^3 \) configurations repel each other while \( d^1 - d^2 \) configurations are attractive. Li\( V_2 \)O\( 4 \) is a metal and therefore the above tetrahedron rule cannot be strictly obeyed. Otherwise a single transition \( d^2 \leftrightarrow d^1 \) would imply a rearrangement of configurations in nearly all tetrahedra. However, we are interested here in the spin excitations only, because of the large entropy associated with the low-energy excitations. Therefore the heavy quasiparticle excitations must involve predominantly spin degrees of freedom. Thus for the present purpose we may assume that the tetrahedron rule is strictly obeyed. In that case the ground state \( |\psi_0\rangle \) of the system is of the form

\[
|\psi_0\rangle = \sum_{n} \alpha_n |\phi_n\rangle \tag{2}
\]

where the \( |\phi_n\rangle \) are all configurations which obey the tetrahedron rule. In each of the \( |\phi_n\rangle \) the \( V^{4+} \) ions form chains and rings. They are surrounded by chains and rings of \( V^{3+} \) ions. An example is shown in Fig. 1. One may check that the smallest rings possible involve six \( d^1 (d^2) \) ions. Ring sizes increase in units of four, i.e., they involve 10,14 etc. \( V \) ions of one kind. The form of the \( \alpha_n \) is irrelevant here and will be the subject of a separate investigation.

Consider the \( d^2 \) ions. Without Hund’s coupling the ratio of \( S = 1 \) triplet and \( S = 0 \) singlet configurations would be approximately 3 : 1. Finite Hund’s coupling enlarges it further. Therefore we deal with \( S = 1 \) chains (and rings) interrupted occasionally by sites with \( S = 0 \).

FIG. 1. Example of a configuration \( |\phi_n\rangle \) obeying the tetrahedron rule. Solid dots: spin \( \frac{1}{2} \) sites; empty dots: spin 1 sites. They form chains and rings each. Notice a ring consisting of six spin \( \frac{1}{2} \) sites in the upper right corner.

Let us assume next that the coupling between \( S = 1 \) and \( S = \frac{1}{2} \) sites would vanish. In that case the excitations of the system are given by those of the \( S = \frac{1}{2} \) chains and rings and of the \( S = 1 \) chains and rings, the
latter being disrupted by $S = 0$ configurations. At low temperatures only the excitations of the $S = \frac{1}{2}$ Heisenberg chains are important because their spectrum goes to zero in the long wave length limit. The excitations of the $S = 1$ Heisenberg chains and rings have a gap in the excitation spectrum and play no role at low $T$. The same holds true for $S = \frac{1}{2}$ rings which are sufficiently small.

The relevant excitations are of the form

$$A_k^+ | \psi_0 \rangle = \sum_n \alpha_n A_n^+ | \phi_n \rangle$$  \hspace{1cm} (3)

where $A_k^+$ generates a spin wave of wavelength $\lambda = \frac{2\pi}{k}$ in the $S = \frac{1}{2}$ chains and large rings contained in $| \phi_n \rangle$. The $S = \frac{1}{2}$ chains and large rings have a much larger statistical weight than the $S = \frac{1}{2}$ small rings and therefore we may assume that half of the $N$ sites are involved in the low energy excitations. The corresponding low-temperature specific heat is

$$C = \gamma T$$  \hspace{1cm} (4)

with $\gamma = \frac{2k_B R}{3J_3}$

where $J_3 = J_{ij}$ when $S(i) = S(j) = \frac{1}{2}$. Note that only one $V$ ion per formula unit is contributing to the low-energy excitations and hence to $\gamma$. The low-temperature spin susceptibility is that of Heisenberg chains and given by 

$$\chi_{sp} \approx 4\mu_{B}^2 R/(\pi^2 J_3)$$  \hspace{1cm} (5)

which results in a Sommerfeld-Wilson ratio of $R_W = 2$.

In the following we want to provide arguments which suggests that the above considerations still apply, when the coupling $J_{ij}$ between sites with spin $S = \frac{1}{2}$ and $S = 1$ is included. For that purpose we must first estimate the relative sizes of $J_{ij}$ when spins $\frac{1}{2}$ and spins 1 are coupled among themselves, i.e., $J_3$ and $J_1$ and when a spin $\frac{1}{2}$ couples with a spin 1, i.e., $J_2$. With this aim we have performed LDA+$U$ band structure calculations in order to estimate their relative sizes. The calculations were performed under the following assumptions. First of all, we assumed that the $V$ ions with $d^1$ and $d^2$ configurations form two different families of ordered chains which alternate in $z$ direction. Both families lie in the $xy$ plane but they differ by a rotation of $\pi/2$. With this arrangement each $V$ tetrahedron is occupied by an equal number of $d^1$ and $d^2$ ions, i.e., the tetrahedron rule is strictly obeyed. It should be noticed that no charge ordering of $V$ ions has been observed experimentally. Nevertheless the chosen configuration serves its purpose. We have found that for such an arrangement of $V$ ions a self-consistent solution can only be obtained for values of the screened on-site Coulomb integral $U$ larger than 3.8 eV, where as the use of smaller values of $U$ leads to a solution with the average $d^{1.5}$ count for each $V$ ion. The value of $U = 4$ eV, that was used in the present work to calculate $J_{ij}$, is larger than the value of about 3 eV previously estimated and the experimental one which is close to 2 eV [23].

However, we believe that the calculated $J_{ij}$ can be used to estimate their relative strengths. In order to calculate the coupling constants we started from a self-consistent solution for a collinear magnetic state with an AF ordering of $d^1$ and $d^2$ ions along the corresponding chains. In this case each $d^1$ ion has two $d^2$ nearest neighbours with the same and two with the opposite orientation of the spin direction, i.e., $d^1 - d^2$ magnetic interactions are frustrated. Then, the band energies of non-collinear magnetic structures with an angle between either the $d^1$ spins or the $d^2$ spins varying from $180^\circ$ to $0^\circ$ were calculated, and $J_{ij}$’s were determined by comparing total energies with those of the corresponding Heisenberg-like model with nearest neighbour interaction. (For a detailed description of the procedure see Ref. [22] and references therein.) As a result we obtained values of 3 meV and 24 meV for the coupling constants $J_3$ and $J_1$, respectively. The coupling of a spin $\frac{1}{2}$ with a spin 1 is intermediate.

Consider first two corner-sharing tetrahedra (see Fig. 2) with spins $S(\nu)$. Let sites 1, 2, 3 have spin $S = 1$ while the remaining sites have spin $\frac{1}{2}$. We introduce $\bar{\Sigma}_1 = S(1) + S(2)$, $\bar{\Sigma}_2 = S(2) + S(3)$, $\bar{\sigma}_1 = S(4) + S(5)$, $\bar{\sigma}_2 = S(6) + S(7)$ in terms of which the interaction Hamiltonian $\sum_{(ij)} J_{ij} S(i) S(j)$ is written

$$H_W = \frac{J_1}{2} [\bar{\Sigma}_1^2 + \bar{\Sigma}_2^2 - 8] + \frac{J_2}{2} [\bar{\Sigma}_1 \bar{\sigma}_2 + \bar{\Sigma}_2 \bar{\sigma}_1]$$

$$+ \frac{J_3}{2} [\bar{\sigma}_1^2 + \bar{\sigma}_2^2 - \frac{3}{2}] .$$  \hspace{1cm} (5)

The ground state has $\sum_1 = \sum_2 = \sigma_1 = \sigma_2 = 0$. When $J_1 \gg J_2, J_3$ the low-energy excitations are given by changing $\sigma_1$ or $\sigma_2$ from 0 to 1, i.e., they are within the spin $\frac{1}{2}$ subsystem. They are unaffected by $J_2$, i.e., the coupling between spin $\frac{1}{2}$ and spin 1 sites. The argument builds on the fact that the coupling $J_1$ between the spin 1 sites is much stronger than the one between the spin

FIG. 2. Two tetrahedra of a spinel structure. Sites $\nu = 1, 2, 3$ have spin $S(\nu) = 1$ while the remaining ones have spin $\frac{1}{2}$.  

sites, i.e., $J_3$. It should hold also when instead of two tetrahedra the whole lattice is considered. The excitations of spin $\frac{1}{2}$ chains and large rings are effected by the $S = 1$ subsystem only via spin flips of the latter. However, the excitations of the $S = 1$ subsystem have a gap and moreover from the LDA+$U$ calculations it follows that $J_1 \simeq 8J_3$. Therefore the low-lying excitations take place within the $S = \frac{1}{2}$ subsystem only. Consequently $\gamma$ is given by that of uncoupled $S = \frac{1}{2}$ chains (or large rings), i.e., by $[\bar{4}]$. Indeed, this reasoning provides for a simple explanation of the heavy quasiparticle excitations found in LiV$_2$O$_4$. In order to explain the experimentally observed value of $\gamma = 0.42 J/mol \cdot K^2$ a coupling constant $J_3/k_B = 13.3K$ is required. This value agrees up to a factor of 2.6 with the value $J_3^{calc}/k_B = 35K$ found from the LDA+$U$ calculations. Furthermore, the observed Sommerfeld-Wilson ratio of 1.7 is relatively close to the theoretical value of $R_W = 2$ found here. Some comments are in order at that point. We cannot expect that a LDA+$U$ calculations give precise values of spin coupling constants, since those physical quantities are rather sensitive to a precise description of correlations (see, e.g., [23]) which would require much more sophisticated computations. Also $\gamma$ as given above may well contain contributions from phonons, i.e., $\gamma = \gamma_0(1+\lambda)$ where $\lambda$ describes the contribution from the electron-phonon interactions. For example, a value of $\lambda = 1$ would double the value of $J_3$ needed for explaining $\gamma_0$ to $J_3 \approx 27K$. But it would also double the experimental value of $R_W$ to 3.4 since $\lambda$ does not contribute to $\chi_{sp}$. The calculated value of $R_W = 2$ is a result for the spin $\frac{1}{2}$ subsystem. Therefore any contribution of the spin 1 subsystem [19] to the measured values of $\chi_{sp}$ must be subtracted before a comparism with experiments is made. Even a small contribution of 15 % reduces $R_W$ from 3.4 to 2.7.

Experiments show no maximum in $\gamma(T) = C(T)/T$ in distinction to theory [18] and a broad one in $\chi_{sp}(T)$ around $T = 16K$. Theory predicts such a maximum at 0.6$J_3$ which would imply a value of $J_3 \approx 27K$.

Although the agreement between theory and experiment is not perfect, which comes to no surprise in view of the simplifications made, we believe to have found a simple physical picture for the hitherto unexplained unusual low-temperature thermodynamic properties of the material.

It is based on the proposition that the system is a superposition of configurations with spaghetti like spin $\frac{1}{2}$ chains and rings. They are well separated from each other since the spin 1 chains and rings surrounding them have a large coupling constant $J_1$ and a gap in the excitation spectrum (Haldane gap). Therefore, the low-energy excitations take place in spin $\frac{1}{2}$ Heisenberg chains only similarly as in Yb$_4$As$_3$. Because of the near separation of spin and charge degrees of freedom LiV$_2$O$_4$ should not be a Fermi liquid in the classical sense. Rather it should show features of a Luttinger liquid because of the presence of an intrinsing chain structure even in the cubic lattice. It would be most interesting to determine the effective masses at the Fermi surface, e.g., by de Haas-van Alphen experiments. We speculate that they should be much smaller than suggested by the large value of $\gamma$. As pointed out above the tetrahedron rule is not expected to hold rigorously. Therefore, the influence of small deviations from it remains an interesting topic which will be investigated separately. The same holds true for the effect of impurities and moreover for doping. Furthermore, it remains to be seen whether similar ideas apply also to LiTi$_2$O$_4$ which is a superconductor at low temperatures or to pyrochlore lattice systems.

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