The electronic structure of the heavy fermion metal LiV$_2$O$_4$

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The electronic structure of the first reported heavy fermion compound without f-electrons LiV$_2$O$_4$ was studied by an ab-initio calculation method. In the result of the trigonal splitting and d-d Coulomb interaction one electron of the d$^{1.5}$ configuration of V ion is localized and the rest partially fills a relatively broad conduction band. The effective Anderson impurity model was solved by Non-Crossing-Approximation method, leading to an estimation for the single-site Kondo energy scale $T_K$. Then, we show how the so-called exhaustion phenomenon of Nozières for the Kondo lattice leads to a remarkable decrease of the heavy-fermion (or coherence) energy scale $T_{coh} \equiv T_K^2/D$ ($D$ is the typical bandwidth), comparable to the experimental result.

Heavy fermion systems are characterized by a large effective quasiparticle mass inferred from the strongly enhanced electronic specific heat coefficient and spin susceptibility at low temperatures \[\gamma\]. Until recently this effect was observed only for f-electron compounds containing lanthanide or actinide atoms. The transition metal oxide compound LiV$_2$O$_4$ is the first reported heavy fermion system without f-electrons \[\gamma\].

LiV$_2$O$_4$ has a face-centered-cubic normal-spinel structure. The formal valence of the V-ions is V$^{3.5+}$ leading to 1.5 electrons/V in the 3d-band. The electronic specific heat coefficient $\gamma(T) = C_e(T)/T$ is extraordinarily large for a transition metal compound ($\gamma(1K) \approx 0.42J/molK^2$), decreasing rapidly with the temperature to $\approx 0.1J/molK^2$ at 30 K. The spin susceptibility from 50K to 400K shows a Curie-Weiss behavior corresponding to weakly antiferromagnetically coupled ($\theta \approx -30$ to -60 K) vanadium local magnetic moments with $S=1/2$ and $g \approx 2$, but static magnetic ordering does not occur above 0.02 K and superconductivity is not observed above 0.01 K. The nearly temperature independent spin susceptibility $\chi(T)$ and Knight shift $K(T)$ for $T < 30K$ are a sign of the disappearance of the V local moment in this temperature region.

In the traditional heavy fermion compounds there are two distinct types of electronic states, the localized f-orbitals of lanthanide or actinide atoms which form local moments and the delocalized s-, p-, d-orbitals which are responsible for the metallic properties. The weak hybridization of the f-orbitals with the conduction states leads to the low temperature anomalies. If one of the 1.5 3d-electrons per V ion would be in a localized orbital, and the rest in a relatively broad band, then the situation would be analogous to f-compounds and all experimental facts could be qualitatively understood. As the general opinion was that these 1.5 electrons are in the (same) band formed by $t_{2g}$-orbitals, such a model was considered to be unrealistic. In this paper we will show that the trigonal point group symmetry of the V ion in LiV$_2$O$_4$ lifts the degeneracy of the $t_{2g}$-band*. As a result the above mentioned model, is appropriate to estimate the heavy-fermion energy scale for this compound.

The normal-spinel crystal structure is formed by the edge-shared oxygen octahedra with V-atoms at the centres and Li-atoms between octahedra. The face-centered-cubic lattice has four V atoms in the unit cell which form a tetrahedron (Fig. 1). The total space group of the crystal is cubic but the local point group symmetry of V-ion crystallographic position is trigonal. The different trigonal axes of every V-atom in the unit cell are directed towards the centre of the tetrahedron.

![FIG. 1. The four V atoms in spinel unit cell with the corresponding oxygen octahedra. The angular distribution of the density of 3d-electrons obtained in the LDA+U calculation (mainly the localized $A_{1g}$ orbitals) is shown.](image)

The octahedral coordination of the oxygen ions around the V results in the strong splitting of d-states into triply
degenerate $t_{2g}$-orbitals with lower energy and double degenerate $e_g$-orbitals with higher energy. The band structure has three well separated sets of bands, completely filled O-2p-band, partially filled $t_{2g}$ band and empty $e_g$ bands. As only partially filled bands are important for the physical properties we will restrict our analysis to the $t_{2g}$ band.

\[ E_{\text{t}} \approx \sqrt{2} eV \] (Fig. 2) and as a consequence the LDA-occupancy of $E_g$ orbital is significantly larger than the corresponding value for $A_{1g}$ orbital. One would expect that after switching on the Coulomb interaction in LDA+U calculation, the orbital whose occupation was larger becomes in the process of the self-consistency iteration, more and more occupied at the expense of all other orbitals and in the end the d-electron will be localized on one of the $E_g$ orbitals. In reality the situation is more complicated. Indeed, the Coulomb interaction energy will be lowered by localization of the electron on any orbital. However the total energy of the solution with the localized electron on $A_{1g}$ orbital is lower than energy of the solution with $E_g$ orbital due to the trigonal splitting. The rotation invariant formulation of the LDA+U method allows the system to choose itself on what particular orbital (or the particular combination of the basis set orbitals) electrons will be localized. If one starts from the LDA orbital occupancies, then at the first stage of the self-consistency iterations the $E_g$ orbital, having larger LDA occupation become localized. However further iterations cause ‘rotations’ in the five-dimensional space of 3d-orbitals leading to the solution with the $A_{1g}$ orbital occupied. The system arrives at this solution independently of the starting point. The total energy as a functional of the orbital occupation matrix has only one minimum and the corresponding LDA+U equations have only one solution.

The separation of the $t_{2g}$-states into the localized $A_{1g}$ orbital and the conduction band $E_g$ orbitals shows that LiV$_2$O$_4$ can be regarded as an analog of f-systems. In order to estimate the strength of the interaction between the localized and the conduction electrons we have defined an effective Anderson impurity model. The partial DOS for $A_{1g}$ orbital obtained in the LDA+U calculation $n_{A_{1g}}(E)$ was used to determine the position of the impurity state $\epsilon_f$ and the hybridization function $\Delta(E)$:

\[ n_{A_{1g}}(E) = \frac{1}{\pi} \text{Im} \{ \epsilon_f + i \Delta(E) \}^{-1} \] (1)

The results are presented on Fig. 2. We then used the LDA+U results as input to estimate the Kondo energy scale for a single site model. To solve this Anderson impurity model we have used a resolvent perturbation theory.
Fig. 3 we estimate for the single-site Kondo temperature \[T_K\] is well-known to reproduce the low-energy scale of the interaction between local moments. We have estimated this value of the intersite exchange coupling parameter from the results of LDA+U calculation using the formula derived as a second derivative of the total energy in respect to the angle between local moments directions. Our calculation gave the value of the double exchange parameter \[J_{dex} = 530 K\].

However, there is another contribution to the interaction between the local moments. The Kondo exchange is between a local moment (electron on the \[A_{1g}\]-orbital) on one site and the spin of the conduction electron (\[E_g\]-orbital) on the neighboring site, because having different symmetry the orbitals do not mix on the same site. As the spins of the \[E_g\] and \[A_{1g}\] electrons on the neighboring site are ‘strongly’ coupled by the Hund interaction, it gives us an effective antiferromagnetic (AF) interaction between local moments on neighboring sites approximately equal to the Kondo exchange parameter \[J_K\]. As a result there is a strong cancellation between these two processes, ferromagnetic double exchange and AF Kondo-induced exchange so that the net exchange interaction is small. Simply subtracting the two terms leads to an estimate \[J_K - J_{dex} \sim 140 K\].

A realistic lattice model for LiV\(_2\)O\(_4\) contains two competing terms which couple the conduction and localized states. These are the onsite Hund’s ferromagnetic coupling and the AF Kondo interaction which couples conduction and localized electrons on neighboring sites. This competition makes difficulties for a first principles treatment. On the other hand, there are several arguments in favor of ignoring the ferromagnetic interactions relative to the Kondo interaction. For a single localized site, it is well-known that the onsite ferromagnetic coupling between conduction and localized states scales to weak coupling limit at low temperatures and so can be ignored. However it could be argued that in the lattice this ferromagnetic coupling scales to the strong coupling limit through the well-known double exchange effect. But as discussed above the double exchange effect is cancelled here by the AF interaction between the localized spins induced by the Kondo effect. Therefore it seems plausible to ignore at least as a first step the ferromagnetic interactions and treat only the AF interaction so that the model is simply a Kondo lattice model. There may be some renormalization of the Kondo exchange parameter, \[J_K\] but for now we ignore that too.

In the Kondo lattice model there is also a competition between the induced AF interactions which favor AF order and the Kondo effect which favors a singlet groundstate. Here, the former are very weak due to the cancellation affects discussed above and as a result we are in the limit where the Kondo effect dominates. This leads to the formation of a heavy-fermion Landau
Fermi liquid with a characteristic temperature scale for the onset of quantum coherence, $T_{coh}$. The exact value of $T_{coh}$ is difficult to estimate but there are a number of strong arguments that $T_{coh} \ll T_K$, the single site Kondo temperature. We summarize these arguments below.

In the single site case, the local moment forms a singlet pair with any conduction electron within an energy $T_K$ of the Fermi energy. We have the picture of a complex screening cloud which delocalizes the impurity at the Fermi level. The resulting non-perturbative ground state is found to be of Fermi-liquid type \cite{[3,4]}, where all the physical quantities depend on $T_K$. In the concentrated Kondo lattice, the number of conduction electrons per site to screen the local moments is of order $n_k = \frac{T_f}{T} \ll 1$. There is a lack of conduction electrons to screen all the spin array at the energy scale $T_K$; this is the well-known exhaustion phenomenon \cite{[12]}. In that sense, a macroscopic singlet ground state should not take place at $T_K$, but rather at a very low temperature $T_{coh}$. To obtain it, we can use the following simple thermodynamical arguments. The condensation energy that we really dispose to screen the (effective) localized spins is: $E_{cond} = N_V n_k T_K$ where $N_V$ is the total number of V-ions (we have one localized 3d-electron per V). In view to stabilize a perfect singlet ground state, this energy must absorb all the entropy of the impurity lattice which is defined as: $S_{tot} = N_V h \ln 2$. Then, the energy scale at which the entropy of the spin array will go to zero can be simply defined as $T_{coh} = E_{cond}/S_{tot} \simeq n_k T_K = T_K^2/D$ \cite{[10]}. For $T \ll T_{coh}$, the prevalent bonds should be formed between local moments and then $T_{coh}$ plays the role of the effective Kondo temperature in the lattice problem \cite{[4]}. It should be noted that these effects predicted by physical arguments could recently be indeed observed in calculations for the periodic Anderson model in the framework of the Dynamical Mean-Field Theory \cite{[9]}. Taking into account the estimations for $T_K$ and $D$, we obtain $T_{coh} \sim 25 - 40 K$, which agrees well with the numerical result for the periodic Anderson model \cite{[9]}. It also seems to be in good agreement with the experimental result in LiV$_2$O$_4$. This should produce an enhanced linear specific heat and Pauli susceptibility which are proportional to $N_V/T_{coh}$, and a (normalized) Wilson ratio $R_W$ which is equal to one \cite{[4]}. Experimentally, $R_W$ is on the order of unity as in conventional heavy-metals \cite{[2]}. In conclusion, our calculations using the LDA+U method give a theoretical justification of a model with one of the 3d-electrons per V localized in a A$_{1g}$-orbital and the remaining 0.5 electron/V in a conduction band state, primarily of $E_g$ symmetry, which has been previously discussed \cite{[3,4]}. This leads to a lattice model with competing onsite ferromagnetic coupling due to the Hund’s rule and nearest neighbor antiferromagnetic coupling due to the Kondo effect. We present arguments that such a model reduces to a Kondo lattice model. Estimates for the temperature scale for the onset of quantum coherence give a small value, much less than the single site Kondo temperature, in agreement with experiments. The low temperature heavy fermion Fermi liquid is strongly correlated and is therefore a good candidate for a transition to unconventional superconductivity, if it can be made perfect enough.

*Note added—Recently an LDA calculation of the electronic structure of LiV$_2$O$_4$ was made by Eyert et al. \cite{[21]} where the partial density of states of $t_{2g}$ band was analyzed using trigonal symmetry but the possibility of orbital polarization of electrons due to the Coulomb interaction was not investigated.

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