Heavy-Fermions in a Transition-Metal Compound: $LiV_2O_4$

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Abstract

The recent discovery of heavy-Fermion properties in Lithium Vanadate and the enormous difference in its properties from the properties of Lithium Titanate as well as of the manganite compounds raise some puzzling questions about strongly correlated Fermions. These are discussed as well as a solution to the puzzles provided.
INTRODUCTION

The properties of LiV$_2$O$_4$ (LiV) for $T \lesssim 20K$ are those of a heavy-Fermi-liquid: the specific heat $C_v \sim \gamma T$ with $\gamma \approx 0.5 J/moleK^2$, Pauli susceptibility $\chi$ with $\chi T/C_v \approx 1.8$, the resistivity $R(T) = R(0) + AT^2$ with $A \sim \gamma^2$ lying on the Kadawoski-Woods plot. These parameters are similar to those in UPT$_3$ and many rare-earth compounds of Ce and Yb. This discovery raises some very interesting issues in our understanding of strongly correlated Fermions.

LiV$_2$O$_4$ (just as LiTi$_2$O$_4$ (LiT)) has the spinel structure with 2 Transition metal (TM) ions per unit-cell in equivalent sites. So, it is a mixed valent compound with equal ratios of $V^{3+}$, which has $S = 1$ and $V^{4+}$ which has $S = 1/2$. At first appearance the Hamiltonian of the system is similar to the Jonkers-Van Santen compounds, like La$_{2-x}$Sr$_x$MnO$_3$ (LMN), which are also mixed valent with ratio $x/(1-x)$ of Mn$^{3+}$ to Mn$^{4+}$. LMN for $x \sim 0.3$ is a ferromagnetic metal, whose properties are well described by the Double-Exchange model. The first question is why does LiV behave so completely differently than (LMN)? Indeed when is the Double-Exchange model valid?

The isostructural neighbor to LiV, LiT is also mixed valent with equal ratio of Ti$^{3+}$ ($S = 1/2$) and Ti$^{4+}$ ($S = 0$). This is an ordinary metal with mass enhancement of $O(1)$. Why then the dramatic difference between TiV and LiV?

The bare hybridization parameters of rare-earth and actinide compounds are typically more than an order of magnitude smaller than the transition metal compounds. The effective mass observed for them is of the right order of magnitude as arising from the Kondo-effect of the moments in f-orbitals. Assuming the mass renormalization in LiV is also a Kondo-effect, why is the effective mass similar to that in the rare-earth and actinide compounds?

A final question of-course is the applicability of the Kondo-effect and associated ideas to compounds like LiV with just one species of electrons. Such ideas have usually been applied to a lattice of (atleast) two kinds of ions, one of which has f-orbitals with well-localised magnetic moments (because the local correlation energy is much larger than the hybridization
energy with the neighbors) interacting with weakly interacting itinerant electrons. In LiV, the same-electrons act as local moments that are Kondo-quenched as well as the electrons that do the quenching.

It is easiest to start with the final question. A mean-field method for correlated Fermions on a lattice has been recently developed by considering the problem in the limit of large-dimensions \[7\], \[8\]. One of the most fruitful applications of the method is to consider 1 ion in a bath whose properties (static as well as dynamic) are determined self-consistently. For the one band Hubbard model, for example, the Hamiltonian coupling the ion to the lattice is simply the Anderson model for local magnetic moments in which the parameters are determined self-consistently \[8\]. From this point of view there is no formal difference in treating the one-band Hubbard model or the multi-band models, with which Heavy-Fermions are customarily treated. While much remains yet to be developed, especially in the question of effective-interaction between ions, the experimental results in LiV may be taken as further validation of this approach. If we adopt this approach, the other questions in the Introductions may be addressed by considering the competition between the Kondo-effect quenching magnetic moments of an impurity embedded in itinerant electrons and the magnetic-interaction between ions favoring the magnetic moments. The difference between the pair of impurity problem and the actual lattice is then usually a difference of numbers (which in practice is always less than an order of magnitude).

**LITHIUM VANADATE AND LITHIUM TITANATE**

The difference of the properties of LiV (mixed valent with \(S = 1\)) and \(S = 1/2\) and LiT (mixed valent with \(S = 1/2\) and \(S = 0\)) is reminiscent of the difference in properties of mixed valent rare-earth compounds of Ce and Yb on the one hand and of Tm on the other \[3\] \[10\]. One of the valences of Ce(\(f^0\)) and of Yb(\(f^{14}\)) is non-magnetic, while both valence states of Tm in TmSe etc. are magnetic (ignoring a small crystal-field splitting). The dominant interaction of mixed valent systems with Hund’s rule energy comparable or
larger than the hybridization energy is Double-exchange. If $S_i$ is the moment of one of the valences and $(S + 1/2)_{j,\text{max}}$ that of the other, then the Double-Exchange Coupling between two ions $i$ and $j$ is

$$\frac{t_{ij}}{2(S + 1)}|S_i + S_j + 1/2|.$$  \hspace{1cm} (1)

If either $S_i$ or $(S + 1/2)_{j,\text{max}}$ is 0, there is no magnetic interaction to leading order. Moreover the effective Kondo-temperature for the mixed-valence problem is just the hybridization width. For the single band problem as in LiT this is less than an order of magnitude smaller than the one-particle bandwidth. This is much larger than any second-order magnetic interactions. This explains why LiT behaves as an ordinary metal with an effective mass enhancement of order unity; i.e. a specific heat coefficient $\gamma$ which is only a few milliJoules/molecm$^2$. The mixed-valent compounds of Ce and Yb have a $\gamma$ of 50 to 100 milliJoules/molecm$^2$ because the bare hybridization parameters of f-electrons are smaller than those of d-electrons by a corresponding amount.

**HEAVY-FERMION BEHAVIOR OF LITHIUM VANADATE**

Why then does LiV not exhibit the properties of the Double-exchange model and be ferromagnetic as LMN and TmSe (when sufficiently mixed valent) do? The answer can be found in the energetics of the successive crossovers that a $S \neq 1/2$ moment must undergo in the Kondo Effect. These can be estimated on the basis of variational calculations reported sometime ago [12]. The variational approach in such problems foreshadowed the so-called no-crossing approximation [13], the $1/N$ approximation [14] and the slave-Boson approximations [15]. The conclusions drawn here could be derived equally well by these methods.

The states of an (orbitally degenerate) mixed valent ($S=1, S=1/2$) impurity in a metal can be a spin-triplet, a spin-doublet or a spin-singlet. the wavefunction for each of these states and their energy is given in Ref. (12). In this case as well as the simpler $S = 1/2$ problem, the Kondo-Temperature which sets the scale for the low temperature properties is
the difference in the binding energy of the singlet and the doublet states. But for the mixed-valent V ion, one must also consider the energy difference of the triplet and the doublet state as well. This difference sets the scale for the crossover to an effective $S = 1/2$ problem. The binding energy of the triplet state is very small compared to that of the doublet and the singlet state, which are very close in energy. So the triplet state can be ignored. The binding energy of the doublet ($k_B T_D$) is of the order of the hybridization energy. The binding energy of the singlet ($k_B T_S$) is lower than that only by $O(10^{-2} k_B T_D)$. The difference in binding energy for these states arise from the different phase-space for scattering allowed in each of the spin-states and has been fully explained in Ref. (12).

Given these energies, it follows that for $T \lesssim T_D$, the properties of a single mixed valent Vanadium impurity are those of the $S=1/2$ problem until a $T = T_F$ of $O(T_D - T_S)$. Below this temperature the properties are that of a Fermi-liquid with an effective Fermi-temperature $T_F$. If $T_D$ is much larger than the double-Exchange parameter, Double-exchange is irrelevant and the (thermodynamic) behavior of the periodic lattice can be calculated from that of a single-site problem.

A reasonable number for the hybridization energy is $O(10^3) K$, i.e. an order of magnitude smaller than the one-electron bandwidth. Then below this temperature the property of the system is that of a $S = 1/2$ problem. These calculations then explain why the heavy-fermion behavior occurs with $T_F$ of about 20K as well as show that the effective magnetic moment above $T_F$ up to a very high temperature is of $S=1/2$ rather than the mean of $S = 1$ and $S = 1/2$. Indeed, the magnetic susceptibility above $T_F$ and below 300K has the Curie-constant corresponding to $S = 1/2$ [1,2]. This is a strong test of the ideas and results presented here.

**DOUBLE-EXCHANGE IN LANTHANUM MANGANITE**

Finally we come to the question of why the Kondo-effect does not eliminate the possibility of ferromagnetism through Double-exchange in LMN. The reason has to do with the details
of the electronic structure of the $Mn^{3+}$ and $Mn^{4+}$ ions. The latter has 3 Hund’s rule coupled electrons in the $t_{2g}$ orbital while the former has another electron Hund’s rule coupled but in the $e_g$ orbitals. The ionization energy to go from the former to the latter is on the scale of $1eV$. While two ions are then degenerate when considering the energetics of Double-exchange, they are not mixed-valent for purposes of the energetics of the Kondo effect. The first stage in the Kondo-effect would be a crossover from a $S = 2$ to a $S = 3/2$. The effective exchange parameter for this is the square of the hybridization energy divided by the ionization energy, which is then an order of magnitude smaller than the hybridization energy. The crossover temperature then is much smaller than the Double-exchange energy favoring the existence of the bare spin-states.

This aspect of the problem is absent in LiV and LiT because the two electronic states are both in the $t_{2g}$ manifold and the exchange energy is simply the hybridization energy.

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