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Heavy fermions in the transition-metal compound LiV_2O_4

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Lithium vanadate is a heavy-fermion metal with a mass enhancement of $O(10^2)$ while its isostructural neighbor, lithium titanate, has a mass enhancement of only $O(1)$. The Hamiltonian for them as well as for the manganites (which are ferromagnetic metals) are the same except for a change of the spins of the magnetic ions. The enormous difference in the properties of these compounds raises some puzzling questions about strongly correlated fermions. These are discussed and a solution is provided. [S0163-1829(99)51430-6]

INTRODUCTION

The properties of LiV_2O_4 (LiV) for $T \lesssim 20$ K are those of a heavy Fermi liquid:[1,2] the specific heat $C_v \sim \gamma T$ with $\gamma \approx 0.5$ J/mole K^2, Pauli susceptibility χ with $\chi T/C_v \approx 1.8$, and the resistivity $R(T) = R(0) + AT^2$ with $A \sim \gamma^2$ lying on the Kadawoski-Woods[3] plot. These parameters are similar to those in UPt_3 and many rare-earth compounds of Ce and Yb.[4] This discovery raises some very interesting issues in our understanding of strongly correlated fermions.

LiV_2O_4 [just as $LiTi_2O_4$ (Ref. 5) (LiT)] has the spinel structure with two 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,[6] like $La_{2-x}Sr_xMnO_3$ (LMN), which are also mixed valent with ratio $x/(1-x)$ of Mn^{3+} which has $S=2$ to Mn^{4+} which has $S=3/2$. 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 (at least) two kinds of ions, one of which has f orbitals with well localized 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 one 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 multiband 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 Introduction 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.[9,10] One of the valences of Ce(f^0) and of Yb(f^{14}) is nonmagnetic, 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 $\mathbf{S}$ is the moment of one of the valences and $(\mathbf{S}+1/2)_{\text{hund}}$ is the Hund's rule-coupled moment of the other, then the double-exchange coupling[11] between two ions at sites i and j is

$$[t_{ij}/(2S+1)]|\mathbf{S}+(\mathbf{S}+1/2)_{\text{hund}}|. \quad (1)$$

Here t_{ij} is the transfer integral which interchanges the valence of the ions at sites i and j. According to Eq. (1), if either $\mathbf{S}$ or $(\mathbf{S}+1/2)_{\text{hund}}$ is zero, there is no magnetic interac-

tion to the 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 γ which is only a few mJ/mole cm^2. The mixed valent compounds of Ce and Yb have a γ of 50–100 mJ/mole cm^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 do LMN and TmSe (when sufficiently mixed valent)? 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 some time 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 ($S = 1, 1/2$) impurity in a metal can be a spin triplet, a spin doublet or a spin singlet. The wave function for each of these states and their energy is given in Ref. 12. These wave functions are written for the case that the Hund's rule coupling for the charge 2 case, leading to the $S=1$ state, is much larger than the hybridization energy. 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 arises 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 20 K, 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 300 K has the Curie constant corresponding to $S=1/2$.[1,2] This is a strong test of the ideas and results presented here.

To substantiate these ideas, especially quantitatively, a dynamical mean-field calculation[7,8] for the model on a lattice is suggested.

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 three Hund's rule coupled electrons in the t_{2g} orbital while the former has another Hund's rule coupled electron but in the e_g orbitals. The ionization energy to go from the former to the latter is on the scale of 1 eV. 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 $S=2$ to $S=3/2$. 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.

SUMMARY

Lithium titanate is a Fermi liquid with mass enhancement of $O(1)$ because it is a mixed valence compound where one of the valences is nonmagnetic and the other has $S=1/2$. The effective Kondo temperature in this case is the order of the hybridization between the magnetic ions. Lithium vanadate is mixed valent with one of the valences with $S=1$ and the other with $S=1/2$. The magnetic moment renormalizations in this case must proceed in two stages, first to an effective $S=1/2$ problem at temperatures of the order of the hybridization energy and second to a nonmagnetic state. Existing calculations for mixed valent impurities provide that the effective renormalization temperature for this is $O(10^{-2})$ that of the former. This explains qualitatively why the effective mass enhancement in this compound is $O(10^2)$. The properties of either of these compounds are quite different from the manganites because in the latter, because of the crystal-field energy separating the ionization level of different valences, the effective moment renormalization scale is much smaller than in the vanadates and the titanates. Then the double-exchange energy favoring a ferromagnetic state governs the low-temperature properties.

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