LiV_2O_4: Frustration Induced Heavy Fermion Metal

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We propose a two-stage spin-quenching scenario for the unusual heavy fermion state realized in the mixed valent metal LiV_2O_4. In this theory, local valence fluctuations are responsible for the formation of partially quenched, spin-$\frac{1}{2}$ moments below room temperature. Frustration of the intersite spin couplings then drives the system to produce the heavy Fermi liquid seen at low temperatures. The anomalous resistivity and the sign change of the Hall constant can be understood naturally within this model, which also predicts a unique symmetry for the heavy quasiparticle bands that may be observed in de Haas–van Alphen experiments.

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Magnetic frustration has attracted increasing attention in recent years as an emerging tool to suppress antiferromagnetism and generate new types of electronic behavior. One exciting possibility is the development of frustration induced heavy electron behavior in d-electron systems where the Kondo temperature is generally too small to overcome magnetic order without frustration. The recognition of heavy fermion behavior in LiV_2O_4 [1] was an important first step in this direction. In LiV_2O_4, the frustrated lattice remains undistorted to the lowest temperatures measured [2]. The heavy electron state which then develops is unusual in many respects: it displays a monotonically increasing resistivity [3], a pressure-driven metal-insulator transition [4], and field independent heat capacity up to 30 T [4].

LiV_2O_4 forms a spinel structure. The magnetic vanadium atoms are homogeneously mixed valent forming a lattice of undistorted corner-shared tetrahedra. The spin at each site fluctuates between $S = 1$ ($3d^2$) and $S = \frac{1}{2}$ ($3d^1$) with a formal valence of 3.5. Antiferromagnetic couplings between these spins [5,6] imply that the lattice is a highly frustrated metal. A strong on-site Hund's coupling between spins of order 1 eV [7] is manifested in the photoemission [8] and the high temperature magnetic susceptibility [6]. At room temperature the magnetic suceptibility and specific heat indicate the presence of spin-$\frac{1}{2}$ local moments at every site [3,9]. Below 4 K, the moments quench into a heavy Fermi liquid [1].

There have been several attempts to explain this physics. One class of model sees the frustration as secondary, the essential physics being due to mixed valence [10], exhaustion [7], 1D chains [11], or a two-band Hubbard model [12]. Another argues that frustration is essential, leading to a tetrahedron rule [13], a frustrated Kondo lattice [14], antiferromagnetically coupled spins Hund's coupled to conduction electrons [15], or quantum criticality [16]. Here we present a simple two-band model which we believe captures the essential physics: a two-stage spin quenching that could not occur in the absence of frustration; and show how our results can be extended to the pyrochlore structure.

The high temperature physics of LiV_2O_4 can be understood as an $S = 1$ Mott insulator doped with holes on a pyrochlore lattice. The strong Hund's coupling leads us to consider only spin-1 and spin-$\frac{1}{2}$ sites coupled antiferromagnetically over the lattice via direct exchange [17],

$$H = -t\sum_{(i,j)}[X_{0\sigma}(i)X_{\sigma 0}(j) + \text{H.c.}] + \sum_{(i,j)} J s_i \cdot s_j, \qquad (1)$$

where $X_{0\sigma} = |\frac{1}{2}, \sigma\rangle\langle 1, \sigma'| = \chi^\dagger b_\sigma$ is a Hubbard operator allowing the charged holes to move in the spin background via a hopping matrix element t, subject to the constraint $b_\sigma^\dagger b_\sigma + \chi^\dagger\chi = 2$. J is an antiferromagentic coupling between nearest neighbor spins. The local physics of this model is that of a mixed valent impurity undergoing charge fluctuations $d^2 \rightleftharpoons d^1 + e^-$ via hybridization with the surrounding bath of holes, as might be formalized in a dynamical mean-field (DMFT) description of the above model. The effective impurity Hamiltonian replacing the first term in H would then be

$$H_1 = \sum_{k\sigma} \epsilon_k c_{k\sigma}^\dagger c_{k\sigma} + \sum_{k\sigma} t(X_{\sigma 0} c_{k\sigma}^\dagger + \text{H.c.}). \qquad (2)$$

From strong coupling arguments [18], we know that a Fermi sea of electrons forms below T_1, quenching the local moment character on each site to $S = \frac{1}{2}$. This provides a natural explanation for the behavior seen below room temperature. On the lattice, this fluid can be visualized as a smooth Fermi sea, from which the residual spin-$\frac{1}{2}$ moments protrude like spines on the hide of a porcupine (Fig. 1). The original antiferromagnetic interaction between nearest neighbor sites now couples the electron sea to the residual spin-$\frac{1}{2}$ moments. The properties of this "porcupine" Fermi sea are the topic of the remainder of this Letter. The question is *what is the nature of the intrasite screening process that removes the free spins (spines) at low temperatures?*

At low temperatures, J becomes an effective Kondo coupling between the localized spins and the newly freed electrons in the Fermi sea. The locally symmetric spin

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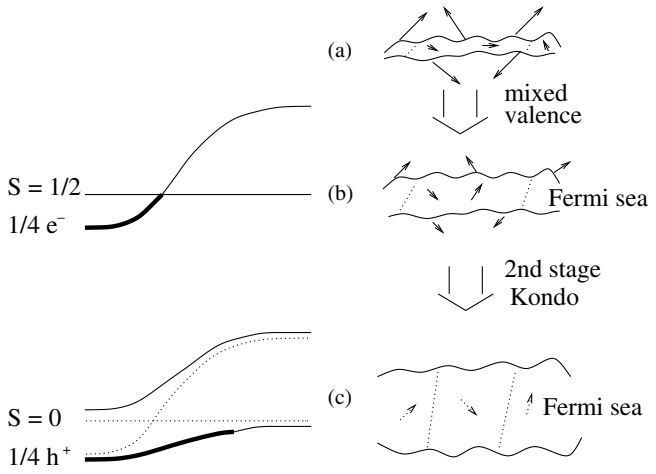

FIG. 1. (a) High temperature phase with large moments. (b) Intermediate temperature phase with underscreened $S = 1/2$ moments embedded in a Fermi sea like the spines of a porcupine (left: corresponding $\frac{1}{4}$-filled band interacting with a localized level). (c) Low temperature phase in which the Heisenberg interaction hybridizes these bands leaving a heavy Fermi liquid of holes (left: corresponding band picture).

state required to satisfy the strong Hund's coupling means that spatial overlap of the realized Wannier states is forbidden as the heavy quasiparticle forms at low temperatures. Thus, even after the complete breakdown of any orbital picture, as the mixed valent spin quenching of the upper level occurs in the totally symmetric channel the second stage spin quenching can occur only in an orthogonal channel. This is the analog of the atomic Hund's selection rule for itinerant states. Thus, the conditions no overlap, no phase transition (equivalent sites), and no time-reversal symmetry breaking arise, uniquely specifying the second channel (Fig. 2). The unusual symmetry of the composite quasiparticles resulting from this second spin quenching should be observable by de Haas–van Alphen experiments.

We now treat the second stage at the mean-field level keeping in mind that for LiV_2O_4, we really want to have a half-filled localized d band interacting with a quarter-filled delocalized d band. Estimates of $J \approx \theta_{\rm cw}^{{\rm high}T} \approx 400$ K [6], $T_{c2} \approx 4$–50 K, and $t \approx 2$ eV [17] (band

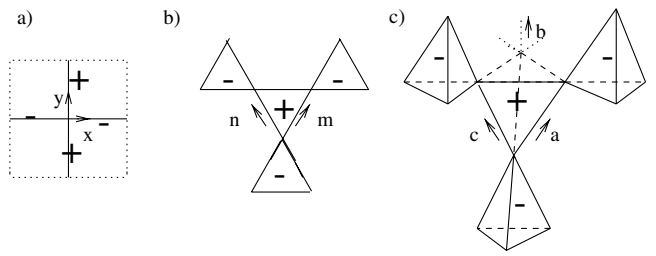

FIG. 2. Symmetry selects a unique symmetry channel for the second-stage Kondo effect in the (a) square lattice (b) Kagomé lattice, and (c) pyrochlore lattice. The ± signs refer to the relative phases of the Wannier state at neighboring sites.

theory) have been made, and we expect that $T_{c1} \propto t$ and $T_{c2} \propto te^{(tb^2)/J}$ as these are the two energy scales in the problem. It is convenient to recast the Hubbard operators into a slave boson language,

$$H = \sum_{\langle ij \rangle} (-tX^i_{0\sigma} X^j_{\sigma 0} + J\mathbf{s}_i \cdot \mathbf{s}_j) - J_H \sum_j \left(\mathbf{s}_j^2 - 2 + \frac{5}{4} X^j_{00} \right), \tag{3}$$

where $X_{0\sigma} = b^\dagger c_\sigma$ is a Hubbard operator allowing the holes to move in the upper e_g' symmetry channel, $\mathbf{s} = \frac{1}{2}(c^\dagger_\alpha \boldsymbol{\sigma}_{\alpha\beta} c_\beta + d^\dagger_\alpha \boldsymbol{\sigma}_{\alpha\beta} d_\beta)$ is the total spin, and we need to enforce the constraints $n_c + n_b = 1$, $n_d = 1$ (a localized spin-$\frac{1}{2}$ level of a_{1g} symmetry). The Hund's coupling J_H is to be taken to infinity to enforce the constraint $S^2 = 2$ at doubly occupied sites.

We now demonstrate how a mean-field treatment of Eq. (3) leads us to the effective Hamiltonian:

$$H_{\rm mf} = \sum_{k\sigma} (C^\dagger_{k\sigma}\ \mathcal{D}^\dagger_{k\sigma}) \mathbf{h}_k \begin{pmatrix} C_{k\sigma} \\ \mathcal{D}_{k\sigma} \end{pmatrix} + 2 \sum_\Gamma \frac{\bar{\Delta}_\Gamma \Delta_\Gamma}{J^\Gamma} + \lambda_1 (|b|^2 - 1) - \lambda_2, \tag{4}$$

where

$$\mathbf{h}_k = \begin{pmatrix} -2t|b|^2 \Phi^{(1)}_k + \frac{\lambda_1 - \mu}{N} & \Delta_\Gamma \Phi^{*(\Gamma)}_k + i\xi \\ \bar{\Delta}_\Gamma \Phi^{(\Gamma)}_k + i\bar{\xi} & \frac{\lambda_2}{N} \end{pmatrix} \tag{5}$$

and $\mathcal{D}^\dagger_k = (d_{1k} \ldots d_{Nk})$, $C^\dagger_k = (c_{1k} \ldots c_{Nk})$ demark the number of bands arising from the magnetic unit cell of the lattice under consideration. λ_1 and λ_2 are Lagrange multipliers fixing the occupancies of the electron and spin liquid. $\Phi^{(\Gamma)}_k$ is an N dimensional matrix representing the Wannier functions, where N is the number of atoms per unit cell and $\Gamma = 1, \ldots, M$ specifies the number of orthogonal channels required to decouple the Heisenberg interaction between one site and its M nearest neighbors.

The mean-field kinetic energy term of H is

$$H_{\rm kin} = -\sum_{\langle ij \rangle} t(c^\dagger_\sigma b)_i (b^\dagger c_\sigma)_j = -2t|b|^2 \sum_k C^\dagger_k \Phi^{(1)}_k C_k, \tag{6}$$

where the bosons take an expectation value, and the Fourier transform happens to give $\Phi^{(1)}_k$, the totally symmetric Wannier state. Magnetic frustration enables us to neglect the normally dominant interaction between the residual spin-$\frac{1}{2}$ moments; however, we must still consider the Kondo coupling between localized and delocalized bands in the expansion of the $Js_i \cdot s_j$ term of Eq. (3):

$$H_J = J \sum_{\langle ij \rangle} \mathbf{s}^d_i \cdot \mathbf{s}^c_j \rightarrow -\sum_{i,\Gamma} \frac{J^\Gamma}{2} (d^\dagger_{i\alpha} \psi_{i\Gamma\alpha})(\psi^\dagger_{i\Gamma\beta} d_{i\beta}), \tag{7}$$

where the operators of the delocalized level have been expanded in terms of orthogonal linear combinations as $\psi^\dagger_{i\Gamma} = \sum_j \phi^{*\Gamma}(j - i) c^\dagger_j$ and $\phi^{*\Gamma}$ is a form factor reflecting the phases at different nearest neighbor sites of i,

reflecting the possible arrangements of $c^\dagger$ on the lattice. This becomes

$$H_J = \sum_{i,\Gamma}\Big[(\Delta_{i\Gamma}\psi^\dagger_{i\Gamma\beta}d_{i\beta} + \bar{\Delta}_{i\Gamma}d^\dagger_{i\beta}\psi_{i\Gamma\beta}) + 2\frac{\bar{\Delta}_{i\Gamma}\Delta_{i\Gamma}}{J^\Gamma}\Big], \tag{8}$$

where we have performed a Hubbard-Stratonovich gauge transformation on the four-fermion term before Fourier transforming to obtain the off-diagonal terms in Eq. (5).

To treat the term of interest from a Hund's coupling:

$$H_H = \frac{J_H}{4}(c^\dagger_\alpha d_\alpha d^\dagger_\beta c_\beta) \to \frac{4}{J_H}\bar{\xi}\xi + i\bar{\xi}d^\dagger_\alpha c_\alpha + ic^\dagger_\alpha d_\alpha \xi, \tag{9}$$

a Hubbard-Stratonovich gauge field has been introduced to decouple the four-fermion term [19]. Before the decoupling, $H_H|S=1\rangle = 0|S=1\rangle$ and $H_H|S=0\rangle = \frac{J_H}{2}|S=0\rangle$, so in the limit $J_H \to \infty$, the $|S=0\rangle$ state will be forbidden. To write Eq. (4) we have taken the limit $J_H \to \infty$. Although this appears to be non-Hermitian, the mean-field values of ξ, $\bar{\xi}$ (independent variables) will also be imaginary so that physical quantities are real.

The free energy can then be expressed as

$$F = -T\sum_{k,\sigma}\mathrm{Tr}[\ln(1+e^{-\beta \mathbf{h}})] + 2\sum_\Gamma \frac{\bar{\Delta}_\Gamma\Delta_\Gamma}{J^\Gamma} + \lambda_1(|b|^2-1) - \lambda_2, \tag{10}$$

where $\mathbf{h}_k$ is the Hamiltonian expressed as a matrix as above. Since $\bar{\xi}$ and $\bar{\Delta}$ both couple to $C^\dagger_\alpha \mathcal{D}_\alpha$, changing one affects the other, such that $\frac{\partial^2 F}{\partial\bar{\Delta}\partial\Delta}\delta\bar{\Delta} + \frac{\partial^2 F}{\partial\bar{\xi}\partial\Delta}\delta\bar{\xi} = 0$. Integration over such fluctuations yields $\frac{1}{J^s} = \frac{1}{J} - (F_{\bar{\Delta}\xi}F_{\bar{\xi}\Delta}/2F_{\xi\xi})$, which guarantees the orthogonality of the second channel. Channels with $F_{\bar{\Delta}\xi} \neq 0$ are effectively removed from consideration. For example, on the square lattice at $\frac{1}{4}$-filling of the upper level, in the absence of the Hund's term, Φ^1 would have the highest T_{c2}, while including the Hund's term the calculated T_{c2} for this channel turns out to be negative. That is, no transition would occur if channels with $F_{\bar{\Delta}\xi} = 0$ did not exist.

To solve for T_{c2}, it is helpful to isolate the interaction contribution to the Green's functions for the delocalized level

$$G_c^{-1} = (G_c^0)^{-1} - \Sigma, \tag{11}$$

where $\Sigma = \mathrm{x}\text{---------}\mathrm{x} = |\Delta_\Gamma|^2\Phi_k^{\dagger\Gamma}(\omega-\lambda_2)^{-1}\Phi_k^\Gamma$ describes the interactions with the localized level. Writing the free energy contribution as $F_{|\Delta_\Gamma|^2} = -T\mathrm{Tr}\ln(G_c^{-1}) + (2|\Delta_\Gamma|^2/J^\Gamma)$ we find,

$$\frac{\partial^2 F}{\partial\Delta_\Gamma\partial\bar{\Delta}_\Gamma}\Big|_{\Delta_\Gamma = i\xi = 0} = \frac{2}{J^\Gamma} + T\sum_{n,k}\mathrm{Tr}[\Phi_k^{\dagger\Gamma}G_c^0G_d^0\Phi_k^\Gamma] = \sum_k\sum_{\alpha=1}^N \frac{f(E_{k\alpha})-f(\lambda_2)}{\lambda_2 - E_{k\alpha}}\eta^\dagger_{k\alpha}\Phi_k^{\dagger\Gamma}\Phi_k^\Gamma\eta_{k\alpha} + \frac{2}{J^\Gamma} = 0, \tag{12}$$

where $E_{k\alpha}$ is the energy of the αth band of the free conduction electron problem and we have projected $\Phi_k^\dagger\Phi_k$ onto the eigenvectors of H_{kin}; μ, λ_1, λ_2 are set by saddle-point evaluations to fix the filling.

On a square lattice, C_4 symmetry means that the possible overlap phases with the nearest four neighbors are $\phi^\lambda = \frac{1}{2}(1, i^\lambda, i^{2\lambda}, i^{3\lambda})$, $\lambda = \{0,\ldots,3\}$. Hopping occurs in the first channel ($\Gamma = 1$) coinciding with the totally symmetric Wannier state $\lambda = 0$. Time-reversal symmetry specifies the d-wave-like $\lambda = 2$ as the second channel ($\Gamma = 2$). The form factors arise as: $\sum_a \phi^{*1}(a)c^\dagger_{i+a} = \frac{1}{2}(c^\dagger_{i+\hat{x}} + c^\dagger_{i-\hat{y}} + c^\dagger_{i-\hat{x}} + c^\dagger_{i+\hat{y}})$, which under Fourier transform defines Φ^1: $\psi^\dagger_{i1} = \sum_k c^\dagger_k e^{-ikx_i}[\cos(k_x) + \cos(k_y)] = \sum_k c^\dagger_k e^{-ikx_i}\Phi^{*1}_k$. Similarly, $\Phi^{*2}_k = c(k_y) - c(k_x)$ are found $\Phi^{*4,3}_k = s(k_x) \pm is(k_y)$ completing the basis.

The effective T_{c_2} is found from

$$\sum_{k\sigma}\frac{f(0)-f(E_{qp})}{E_{qp}}\Phi^{*2}_k\Phi^2_k + \frac{2}{J} = 0, \tag{13}$$

where $E_{qp} = -2t|b|^2\Phi^{(1)}_k + \lambda_1 - \mu$ is determined self-consistently subject to the conditions $\lambda_2 = 0$ and $\sum_k n_f(-2t|b|^2\Phi^{(1)}_k + \lambda_1 - \mu) = \frac{1-|b|^2}{2}$.

On the pyrochlore lattice, four bands and six nearest neighbors imply 24 independent symmetry channels. The requirement that the states preserve the equivalence between sites reduces this number to 6, given by

$$\phi^\pm_\alpha = \frac{1}{\sqrt{6}}(1, \alpha, \alpha^2, \pm 1, \pm\alpha, \pm\alpha^2),$$

where $\alpha^3 = -1$. Of these, the only state orthogonal to the original channel and time-reversal invariant is $\phi^- = \frac{1}{\sqrt{6}}(1,1,1,-1,-1,-1)$, uniquely specifying the second channel. This particular Wannier state has the property that it changes sign between neighboring tetrahedra on the lattice, as illustrated in Fig. 2. The four by four matrix $\Phi^{(1)}_k$ now has the following parts ($k_{ij} = k_i - k_j$):

$$\Phi^{(1)}_k = \begin{pmatrix} 0 & c(k_a) & c(k_b) & c(k_c) \\ c(k_a) & 0 & c(k_{ab}) & c(k_{ac}) \\ c(k_b) & c(k_{ab}) & 0 & c(k_{bc}) \\ c(k_c) & c(k_{ac}) & c(k_{bc}) & 0 \end{pmatrix}, \tag{14}$$

while

$$\Phi_k^{(2)} = i \begin{pmatrix} 0 & s(k_a) & s(k_b) & s(k_c) \\ -s(k_a) & 0 & s(k_{ab}) & s(k_{ac}) \\ -s(k_b) & -s(k_{ab}) & 0 & s(k_{bc}) \\ -s(k_c) & -s(k_{ac}) & -s(k_{bc}) & 0 \end{pmatrix}. \quad (15)$$

For this case, the free hopping Hamiltonian has been treated previously by Reimers *et al.* [20] There are two flat bands lying above two dispersing bands. Strictly speaking, since we have $\frac{1}{2}$ an electron per site involved and four sites, this would actually give us an insulator. However, since we have dropped the second degenerate band, a more reasonable band structure would likely include band crossings and incomplete fillings of the levels along the lines of Singh *et al.* [17].

A large body of experimental work has been done, and we now discuss a simple interpretation of some of this work. We have four localized half-filled electron bands interacting via a Kondo-like hybridization with four itinerant levels, each quarter-filled, which leaves us with a holelike Fermi surface below T_{c2}. In this way, our model is consistent with the sign change in the Hall constant observed at 50 K in single crystal samples [3]. A simple phenomenological fit consistent with the ideas we have introduced for the resistivity yields

$$\rho = \begin{cases} \rho_i + A_h T^2 & T < 2 \text{ K}, \\ \rho_o + \gamma_{ph} T + A_p T^2 & T > 100 \text{ K}, \end{cases} \quad (16)$$

where $\rho_i = 21\ \mu\Omega\,\text{cm}$ (impurity scattering in the single crystal), $A_h = 2.0\ \mu\Omega\text{cm}\,\text{K}^{-2}$ (arises from the heavy Fermi liquid) as given in Ref. [2], and $\rho_o = 0.27\ m\Omega\,\text{cm}$ (impurity scattering from the localized spin $\frac{1}{2}$), $\gamma_{\text{ph}} = 1.1\ \mu\Omega\text{cm}\,\text{K}^{-1}$ (phonon contribution above θ_D), and $A_p = 2.7 \times 10^{-3}\ \mu\Omega\text{cm}\,\text{K}^{-2}$ (arising from the porcupine Fermi sea) have been extracted from Urano *et al.*'s data [3]. Since $\frac{A_h}{A_p} \approx (\frac{m_h^*}{m_p^*})^2$, this yields an effective mass ratio of $\frac{m_h^*}{m_p^*} \approx 27$. An analogous fit of the magnetic susceptibility, where the $S = \frac{1}{2}$ ($\theta = 66$ K, $g = 2.21$) contribution has been first subtracted away from the high temperature susceptibility measurements [3,6,9,21] leaving a T linear contribution

$$\chi T = \begin{cases} \chi_h T & T < 2 \text{ K}, \\ \chi_p (T - 350 \text{ K}) + \frac{2N_A(\mu g)^2 S(S+1)T}{k_B(T+\theta)} & T > 400 \text{ K}, \end{cases} \quad (17)$$

yields $\frac{\chi_h}{\chi_p} \approx \frac{m_h^*}{m_p^*} \approx 29$. The observed low temperature metal-insulator transition is hardly surprising under pressure as broken symmetry Wannier states lie close in energy to the chosen ϕ^2 for the second channel. Invariance of the heat capacity to 30 T indicates that the magnetic coupling J driving the spin quenching is of much higher energy than the Kondo temperature $T \approx 50$ K.

In conclusion, we have presented a physical picture within which one can understand the physics of the frustrated heavy fermion LiV_2O_4. A simple t-J model is capable of describing both the high temperature mixed valent phase and the low temperature coupling between a Fermi sea and spin liquid. We have been able to uniquely identify the symmetry of the low temperature quasiparticles. Our picture gives a simple qualitative interpretation of the unusual resistivity, the change in sign of the Hall resistance observed and should be used to predict the result of de Haas–van Alphen experiments yet to be performed. This work should serve as a starting point for a DMFT or band structure calculation which might describe the detailed energetics involved. In particular, it would be interesting to follow the compression of the lattice and see how the second channel symmetry depends on nearest neighbor distance.

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