Formation of heavy fermion state in geometrically frustrated LiV$_2$O$_4$

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Outline

Introduction:
- Geometrical Frustration in Spinel Oxides

Heavy Fermion Oxide LiV$_2$O$_4$:
- heavy fermion formation: experimental evidences
- origin of heavy quasi particle mass
  close proximity to charge ordered state
  low-E quasi-particle DOS singularity (meta-magnetism)

Summary & Conclusion
Spinel Structure: $\text{AB}_2\text{O}_4$

(cubic: Fd3m)

LiV$_2$O$_4$ crystallizes in cubic spinel structure
What do we expect for spinel oxides?

- Spin Frustration (when AF)
  
  Strong degeneracy 3D spin liquid?

- Charge Frustration (when mixed valent)
  
  Verway problem  
  Magnetite $\text{Fe}_3\text{O}_4$ 1:1 Fe$^{2+}$ & Fe$^{3+}$

- Orbital Frustration?

- Exotic Phase (transition) ?

  Nature always tries to suppress the degeneracy 
  couple with lattice, orbital, itinerant carriers
Spin Ordering in geometrically frustrated spinel oxides ZnV$_2$O$_4$ ($V^{3+}$) – coupling with orbital & lattice

ZnV$_2$O$_4$: $t_{2g}^2$, $S=1$ Mott Ins.

AF triggered by Cubic to Tetragonal transition at $T_S=50$ K

Orbital ordering of $yz$ & $zx$ orbitals \( \Rightarrow \) suppress frustration

$T_N = 40K$

$\langle \theta_{CW} \rangle = -420K$

$T_N / |\theta_{CW}| = 0.095$

Motome & Tsunetsugu (04)
Charge ordering in geometrically frustrated $\text{AlV}_2\text{O}_4$ ($V^{2.5+}$) – valence skipping state

3:1 $V^{2+}$ and $V^{4+}$ (valence skipping)

instead of 1:1 $V^{2+}$ and $V^{3+}$ (frustrated)

Matsuno, H.T et al. JPSJ (01), PRL (03)

3-1 Charge Ordering coupled with Rhombohedral Distortion below 700 K
LiV$_2$O$_4$ spinel: Verway system without charge ordering

$V^{3.5+}$, mixed valent oxide with 1:1 $V^{3+}$ & $V^{4+}$
(3d$^{1.5}$ 1.5 electron /V $t_{2g}$ $V^{3.5+}$)

Analogous to AlV$_2$O$_4$, & ZnV$_2$O$_4$:
strong charge & spin frustration anticipated

(System does not do anything to suppress frustration)
No charge & spin ordering observed down to the lowest T measured

The first heavy fermion oxides: S.Kondo et al. PRL (97)
Heavy Fermion oxide LiV$_2$O$_4$

\[ \gamma = 380 \text{ mJ/molK}^2 \]

\[ m^* = 150m_0 \]

\[ RW = 1.7 \]

\[ T^* = 20-30 \text{ K} \]

C. Urano, H.T et al PRL 85, 1052 (00)
Origin of the heavy quasiparticle mass?

*Only $t_{2g}$ electrons involved*

- **Kondo Scenario?**
  - 1.5 d-electron
  - LDA+U (Anisimov et al.)
  - $0.5 \, e_g$ (itinerant) + $1 \, a_{1g}$ (localized)
  - trigonal field splitting

- **Geometrical frustration?**
  - A. George
  - P. Coleman
  - P. Fulde
  - a new route to HF

Experimentally:

- critically close to charge ordered insulator (charge frustration)
- no magnetic ordering (spin frustration)
“Bad metal” behavior in LiV$_2$O$_4$

analogous to TMOs near Mott(CO) transition, indicative of close proximity to CO

Distinct from conventional HFs

absence of resistivity saturation

Metallic behavior above IR limit

C.Urano, H.T et al PRL 85, 1052 (00)
Switching from HF metal to Charge Ordered Insulator - HF is a “melted” COI

Pressure induced metal-insulator transition

Very likely CO transition because of the mixed valent nature (formally 1:1 V$^{3+}$, V$^{4+}$)

Geometrical frustration

HF is “Melted” COI
**Evolution of C(T) from frustrated magnet to HF**

ZnV$_2$O$_4$:
strongly frustrated AF
Strong spin degeneracy suppressed by coupling with lattice & orbital

**Hole Doping**
ZnV$_2$O$_4$ + 1/2 hole/V = LiV$_2$O$_4$

$x$-independent large entropy $S(50K) \sim 50\% R \ln 3 / V$
A naive & speculative picture

- Fermi liquid critically close to COI (charge frustration)
  - close proximity to COI leads to quasi-particle DOS (mass) enhancement?

- no magnetic ordering due to spin frustration
  - quasi-particle DOS (mass) not suppressed unlike other SCES without strong frustration
Single crystals of LiV$_2$O$_4$ grown by flux technique

Better understanding of low E quasi-particle electronic states

Matsushita (ISSP)
Meta-magnetic transition at ~40T in LiV$_2$O$_4$ at low T

$M = 1.2 \ \mu_B$

$\Delta M \sim 0.4 \ \mu_B$

- 3 $\mu_B$ for all $t_{2g}$ spins
- 2 $\mu_B$ for $a_{1g}$ spin
- Continue to increase above Hc (no plateau)

Typical of itinerant metamagnetism
**Metamagnetic transition linked with heavy QP formation**

“Metamagnetism” observed only $T \ll 20\, \text{K} = T^*$

MR peak at metamagnetic transition

Critical scattering
**Metamagnetic transition in CeRu$_2$Si$_2$**

\[ \chi \text{ Susceptibility peak} \]

\[ \Delta \rho/\rho \text{ MR peak at metamagnetic transition} \]

**M** Metamagnetism only in coherent regime

Stoner Free Energy (GL) +Zeeman shift for itinerant meta-magnet
Itinerant meta-magnetism

Stoner Free Energy (GL)
\[ F(M) = AM^2 + BM^4 + CM^6 + \ldots - \mu_B HM \]
\[ A = 1 - \alpha < 0 : \]
Stoner condition for FM
A > 0, B < 0, C > 0:
meta-magnetism

\[ B \not\in (D'/D)^2 - D''/3D < 0 \]
\[ D' = dD/dE|_{E_F} \quad D'' = d^2D/dE^2|_{E_F} \]

DOS singularity near \( E_F \)

“Kondo” peak
Right above \( E_F \)
DOS singularity
LiV$_2$O$_4$ as an itinerant meta-magnet

$\chi(T)$ peak temperature $T_{\text{max}}$ and $B_c$ for metamagnetism

Sakakibara (ISSP)

LiV$_2$O$_4$: $T_{\text{max}}$ at 25 K & $B_c$ at 40T

DOS singularity like Kondo peak at a few meV scale!!
PES data from Shin group
- indication of sharp DOS peak above $E_F$

Metamagnetic transition at 40T

$\chi(T)$ peak at 25 K

$\sim 4$ meV
Sharp qp DOS peak ~4 meV above $E_F$ rapidly evolves at low T

reminiscent of Kondo resonance peak in Ce compound

Ce compound: peak slightly above $E_F$ because of degeneracy of f-orbitals

LiV$_2$O$_4$: $t_{2g}$ ?? No reason peak should be slightly above $E_F$ even if kondo

QP DOS enhancement due to close proximity to COI + "XX (additional ingredient)" ??

Which scenario can explain the DOS peak reasonably?
Summary & Conclusion

- Heavy fermion ground state in geometrically frustrated LiV$_2$O$_4$

- Close Proximity to Charge Ordered State

- Sharp Dos peak a few to several meV above the Fermi level

- Needs theoretical input