Heavy Fermion Behaviors in LiV$_2$O$_4$

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Experiments of various types on the metallic transition metal oxide compound LiV$_2$O$_4$ with the fcc normal-spinel structure are reviewed. The low-temperature $T \lesssim 10$ K data consistently indicate heavy fermion (HF) behaviors characteristic of those of the heaviest-mass $f$-electron compounds. A crossover is observed above $\sim 50$ K in the magnetic susceptibility, $^7$Li spin-lattice relaxation rate and neutron magnetic scattering function to a magnetic state variously described as an antiferromagnetically-coupled local-moment metal or, at the opposite extreme, as an itinerant nearly-ferromagnetic metal. Recent theoretical investigations to understand these properties of LiV$_2$O$_4$ are discussed.

Keywords: Heavy fermion behaviors, LiV$_2$O$_4$

I. INTRODUCTION

The phenomenology of heavy fermion (HF) behaviors in systems containing nearly localized $f$-electron lanthanide and actinide atoms is by now well-developed. These include $f$-electron intermetallics with heavy Fermi liquid ground states [1] or non-Fermi liquid ground states [2]. The HF $f$-electron compounds (e.g., CeAl$_3$, UPt$_3$) have enormous electronic specific heat coefficients $\gamma(T) \equiv C_v(T)/T \sim 1$ J/molK$^2$, where $C_v(T)$ is the temperature $T$ dependent electronic specific heat, from which quasiparticle effective masses of several hundred times the free electron mass have been inferred. In such systems a high and narrow ($\sim 10$ meV) peak occurs at low $T$ in the quasiparticle density of states $D$ near the Fermi energy $E_F$, a many-body effect [1]. The large $D(E_F)$ is reflected in a large nearly $T$-independent magnetic spin susceptibility $\chi^{spin}$ and $\gamma$ compared with the predictions of conventional band structure calculations [1]. The normalized ratio of these two quantities, the Wilson ratio $R_W$, is on the order of unity as in conventional metals, where for spin $S = 1/2$ quasiparticles this ratio is $R_W \equiv \pi^2 k_B^2 \chi^{spin}/3\mu_B^2 \gamma$, $k_B$ is Boltzmann’s constant and $\mu_B$ is the Bohr magneton. However, at higher $T$ the $D(E)$ peak height decreases strongly [1], on the scale of a low characteristic temperature $\sim 1$--100 K. This results in a corresponding strong decrease in $\gamma$ and $\chi^{spin}$ with $T$. HF behaviors are not expected for $d$-electron compounds because of the much larger spatial extent of $d$ orbitals than of $f$ orbitals and the resulting stronger hybridization with conduction electron states. Recently, however, HF behaviors, characteristic of those of the heaviest mass $f$-electron HF systems, have been found [1] in the metallic transition metal oxide compound LiV$_2$O$_4$.

LiV$_2$O$_4$ has the face-centered-cubic normal-spinel structure (space group Fd$3$m) [2], and is formally a $d^{1.5}$ system. The Li atoms occupy tetrahedral holes and the V atoms octahedral holes in a nearly cubic-close-packed oxygen sublattice. All V atoms and sets of any chosen clusters of V atoms in LiV$_2$O$_4$ are respectively crystallographically equivalent. This crystallographic feature, together with the non-integral oxidation state of the V atoms, result in metallic character simply due to symmetry considerations. Since the structure remains undistorted down to low ($4$ K) $T$ [2], the compound must remain metallic upon cooling to such temperatures. To our knowledge, the only other spinel-structure transition metal oxide which remains metallic to low $T$ is isostructural LiTf$_2$O$_4$, which is a superconductor below $T_c \leq 13.7$ K [2]. On the other hand, the magnetic susceptibility $\chi(T)$ (4.2--308 K) of LiV$_2$O$_4$ was initially found to be the sum of a $T$-independent term and a Curie-Weiss term $C/(T - \theta)$ due to local V magnetic moments [5]. The Curie constant $C$ is consistent with a V$^{4+}$ spin $S = 1/2$ with $g$-factor 2.23, suggesting that one of the 1.5 $d$-electrons/V atom is (nearly) localized on the atom. The negative Weiss temperature $\theta = -63$ K indicates antiferromagnetic (AF) V spin interactions, and the anomalously large $g$-factor suggests ferromagnetic interactions between the local moments and the conduction electrons [3]. No evidence for magnetic ordering above 4.2 K was found. The local moment behavior strongly contrasts with the relatively $T$-independent Pauli paramagnetism of LiTf$_2$O$_4$ [3].

The metallic character of LiV$_2$O$_4$ together with the above evidence for local moment magnetism motivated the experiments which led to the discovery [3] of HF behaviors in this compound. In particular, we reasoned that due to the geometric frustration for AF ordering inherent in the V sublattice of the structure, perhaps long-range magnetic ordering would be completely suppressed. In this case, a potentially interesting and unusual ground state would be expected. In the following section, the experimental results which have established the HF character of LiV$_2$O$_4$ at low $T$, and a crossover to a different magnetic state above $\sim 50$ K, will be reviewed. Then recent theoretical studies to understand these behaviors will be briefly discussed followed by concluding remarks.
II. REVIEW OF EXPERIMENTAL RESULTS

When screening materials for HF behaviors, the initial experiments are usually specific heat at constant pressure $C_p(T)$ and $\chi(T)$ measurements, and also resistivity $\rho(T)$ measurements. In the case of LiV$_2$O$_4$, single crystals were not initially available and $\rho(T)$ measurements on polycrystalline oxides are notoriously unreliable quantitatively. Before beginning detailed $\chi(T)$ and $C_p(T)$ measurements, we needed to confirm that the Curie-Weiss $\chi(T)$ behavior cited above, which was observed from 300 K down to 4 K, was intrinsic to the material. After an extensive synthesis effort to reduce the concentration of paramagnetic defects, we found that it was not. The $\chi(T)$ does show a Curie-Weiss-like behavior from 400 K down to $\sim$ 50 K, with $C$ and $\theta$ parameters similar to those cited above, but the intrinsic $\chi(T)$ was found to level off below 30 K, showing a weak broad maximum at $\approx 16$ K [3][11]. This intrinsic behavior of high magnetic-purity samples was found independently by two other groups [11][2]. Zero-field-cooled and field-cooled magnetization $M$ measurements in low ($\sim 100$ G) magnetic fields $H$ showed no hysteresis above 2 K, indicating that the broad peak in $\chi(T)$ is not due to static short-range spin-glass ordering [3][11]. Positive muon spin rotation/relaxation $\mu$SR measurements on one of the highest purity polycrystalline samples showed no evidence for static magnetic ordering above 0.02 K [3]. A sample with a significantly higher magnetic impurity level showed static spin-glass-type ordering at about 0.8 K. $\rho(T)$ measurements on a polycrystalline pellet down to 0.01 K showed no evidence for superconductivity [3].

$C_p(T)$ measurements have been carried out on a variety of polycrystalline LiV$_2$O$_4$ samples [3][13]. The highest magnetic purity samples, which have magnetic impurity concentrations corresponding to less than 0.1 mol% of $S = 1/2$ impurities, yielded $\gamma(1K) \approx 0.42$–$0.43$ J/mol K$^2$, which is the largest value observed for any metallic nonmagnetic $d$-metal compound. The effective mass of the quasiparticles, assuming a single spherical band model and a carrier concentration of 1.5 electrons/V atom, is about 180 free electron masses. The Wilson ratio is $R_W \approx 1.7$ assuming quasiparticles with $S = 1/2$ and $g \approx 2$. These results are consistent with a heavy Fermi liquid picture at low $T$. The $C_v(T)$ was determined by subtracting the lattice specific heat contribution (that determined for LiTi$_2$O$_4$ from $C_p(T)$). $\gamma(T)$ decreases rapidly with $T$ up to $\approx 30$ K, then decreases much more slowly up to 108 K. $C_p(T)$ measurements on single crystals confirmed the above low-$T$ behavior [14]. Polycrystalline samples with significantly larger magnetic impurity concentrations showed an increase in $C_p(T)$ with decreasing $T$ below 4 K [3][13] instead of leveling off with decreasing $T$ as in the purest samples.

The linear thermal expansion coefficient $\alpha(T)$ of LiV$_2$O$_4$ was first measured using high resolution neutron diffraction from room temperature to 4 K [3]. These measurements showed normal behavior above 60 K, but below this temperature $\alpha(T)$ became nearly independent of $T$, and then below 20 K $\alpha(T)$ strongly increased again with decreasing $T$ down to 4 K. The low-$T$ results are qualitatively as expected on the basis of the known f-electron HF phenomenology. High resolution $\alpha(T)$ measurements were subsequently carried out using differential capacitance dilatometry [3] which confirmed the neutron diffraction results. From the $\alpha(T)$ and $C_p(T)$ data on the same sample, the Grüneisen parameter $\Gamma(T) \sim \alpha(T)/C_p(T)$ was determined from 4 K to 108 K [13]. At the lowest $T$, the lattice contribution to $\Gamma(T)$ becomes negligible compared to the electronic contribution $\Gamma_e(T)$. The $\Gamma(T)$ increases rapidly with decreasing $T$ below $\approx 20$ K, extrapolating to $\Gamma_e(0) \approx 11.4$, which is intermediate between those of conventional nonmagnetic metals and f-electron HF compounds. Thus these measurements have identified two additional thermodynamic quantities in LiV$_2$O$_4$, the electronic contribution to the thermal expansion coefficient and the electronic Grüneisen parameter, which have $T$ dependences similar to those in heavy-mass f-electron HF compounds.

The spin dynamics in LiV$_2$O$_4$ has been investigated using $^7$Li nuclear magnetic resonance (NMR) measurements [3][2][5][13]. The spin-lattice relaxation rate $1/T_1(T)$ shows a broad maximum at 30–50 K and becomes nearly independent of $T$ from 500 K to 800 K. These high-$T$ data above 50 K were interpreted by one group as indicating that at high $T$, LiV$_2$O$_4$ is a nearly ferromagnetic metal [13], whereas another group including the present author interpreted the data as indicating that this compound is at the opposite end of the localized-itinerant magnetism spectrum, namely a metal containing nearly localized magnetic moments [10]. A study of $1/T_1(T)$ from 1.5 K to 4.2 K for five samples with different magnetic impurity concentrations showed a robust proportional dependence of $1/T_1$ on $T$ [3][13][14]. The slope for the purest samples, $1/T_1(T) \approx 2.25$ sec$^{-1}$ K, is about 4100 times greater than in LiTi$_2$O$_4$, consistent with a HF interpretation. The Korringa ratio, $R_K = K^2T_1T/S_{Li}$ where $K$ is the Knight shift and $S_{Li}$ is a constant, was found in this $T$ range to be about 0.6, i.e., on the order of unity as expected for a Fermi liquid.

The spin dynamics has also been investigated using quasielastic neutron scattering measurements on a polycrystalline sample of LiV$_2$O$_4$ [13]. The quasielastic linewidth $\Gamma$ at 15 K was found to be independent of scattering wavevector, with a finite magnitude for $T \rightarrow 0$. With increasing $T$, $\Gamma$ first showed a minimum at about 10 K, then increased approximately as $\sqrt{T}$. These are characteristic features of conventional f-electron HF compounds. Above $\sim 40$ K, a dramatic crossover in the dynamical structure factor $S(Q,\omega)$ was found, indicative of a different type of metallic state which the authors
interpreted as a possible nearly ferromagnetic metal, in agreement with the conclusion of Ref. [13].

Single-crystal ρ(T) and Hall effect measurements have been carried out to low (0.3 K) temperatures [14]. The ρ(T) data show a T² dependence at low T, with a large coefficient, as expected for a HF Fermi liquid.

High-field M(H) measurements on high-purity polycrystalline LiV₂O₄ were performed in static H up to 20 T and in pulsed H up to 60 T [15]. From 0.6 K to 50 K, M ∝ H up to about 17 T, with a slope vs T in agreement with the χ(T) data. Upon further increasing H at 0.6 K, M(H) shows positive curvature and then a sharp inflection point at H_c = 42 T suggestive of a phase transition. At even higher fields, H ≥ 50 T, M(H) exhibits a plateau with M ≈ 0.6 μ_B/V atom. This M is less than the d³ local-moment value of ≈ 1 μ_B/V atom.

Characteristic temperatures T* associated with the various HF behaviors in LiV₂O₄ can be obtained from the respective measurements discussed above. The ρ(T) data for single crystals [1] exhibit a smooth but pronounced downturn upon cooling below T* ≈ 30 K. The smooth maximum in χ(T) occurs at T* ≈ 16 K [11]. An analysis of the C₆(T) data in terms of the single-ion Kondo model leads to T* = 26.4 K [10,13]. Similarly, the entropy relation γ(T = 1 K)T* = 2R ln 2 (R is the molar gas constant and the prefactor of 2 comes from 2 V atoms per formula unit) yields T* = 27 K. Strong upturns with decreasing T in γ(T), α(T)/T and in the electronic Gruneisen parameter occur below T* = 20–30 K [12,13]. Equating the magnetic field energy μ_BH_c at the inflection field H_c in the high-field M(H) measurements at 0.6 K with μ_BT* gives T* = 28 K [11]. In contrast to the above values of T*, from the quasielastic neutron scattering measurements a much lower Kondo-lattice temperature T* ≈ 5–10 K has been inferred [17].

III. RECENT THEORY

In an ionic picture, the five-fold 3d orbital degeneracy of the isolated V atom is lifted in LiV₂O₄ due to the nearly cubic crystalline electric field (CEF) seen by the V atoms, yielding a ground triply-degenerate t₂g manifold and an excited doubly-degenerate e_g manifold separated by ∼ 2 eV. The slight trigonal distortion of the cubic CEF in the actual structure slightly splits the ground t₂g triplet into an E_g doublet and an A₁g singlet.

Four LDA band structure calculations have been reported for LiV₂O₄ [14,15]. The calculations consistently show a metallic ground state. The ionic picture just described is strongly reflected in the band structure. E_F lies within bands derived from the t₂g orbitals; these bands are separated from those derived from the e_g orbitals by an energy of ≈ 1 eV. The O 2s and 2p bands are filled, lying below the t₂g bands, whereas the Li 2s bands far above E_F are empty, consistent with a −2 oxidation state of O and a +1 oxidation state of Li in the ionic picture. The slight splitting of the E_g- and A₁g-derived bands is not readily discernible in the band calculations. From the band calculations [20,22], the D(E_F) ≈ 7.2 states/eV formula unit is about a factor of 25 smaller that the experimental value inferred from Cᵢᵥ(T) at low T, indicating that electron correlation effects are important in LiV₂O₄.

Electron correlation effects have been discussed using several ideas and approaches. For example, Eyert et al. [13] favor a model in which the geometric frustration for AF ordering of local V moments leads to a large enhancement of spin fluctuations at low T, in turn resulting in heavy-mass quasiparticles. This is a very different picture than for conventional f-electron HF compounds, in which hybridization of local-moment orbitals with those of the conduction electrons lead to mass enhancement via a many-body effect. Anisimov et al. [21] have investigated a model [10,13,14] of the latter type in which one of the 1.5 d-electrons/V atom is localized in the A₁g orbital due to electron correlation effects, with the remaining 0.5 d-electron/V atom being itinerant in broad E_g-derived bands, leading to the observed metallic character. In such a model, ferromagnetic double exchange between the local moments would be important and the outstanding question would then be why LiV₂O₄ is not a metallic ferromagnet at low T [21,23]. Anisimov et al. found that within the LDA+U approach one electron is indeed localized in an A₁g orbital on each V atom. The effects of double exchange were found to be largely canceled by an off-site AF Kondo-like exchange. They solved an effective Anderson impurity model, which when combined with the “exhaustion phenomenon” of Nosé, led to a Kondo lattice model with a coherence temperature T* comparable to the experimental values.

Much progress has been made theoretically to understand the properties of LiV₂O₄. Quantitative calculations of the T dependences of physical observables and comparisons with experimental results will ultimately determine which of the current views of electron correlation effects in LiV₂O₄ are most appropriate.

IV. CONCLUDING REMARKS

In this review we have referred always to heavy Fermi liquid behaviors of LiV₂O₄ at low T, i.e. within the T ranges of the various measurements, and not to a heavy Fermi liquid ground state. It is of course possible that the intrinsic ground state is not a Fermi liquid.

There is no theoretical consensus yet about the mechanism(s) for the low-T HF behaviors of LiV₂O₄. In addition, a theoretical description of the crossover to the high-T behaviors starting at 30–50 K remains to be given. The origin of the high-T behaviors themselves remains to be clarified, in particular whether this compound should
be more appropriately thought of at high temperatures as being an itinerant nearly ferromagnetic metal or a metal containing nearly localized magnetic moments. These states lie at opposite ends of the localized vs itinerant magnetism spectrum. Perhaps the correct view is somewhere in between.

Several features of LiV$_2$O$_4$, some of which were discussed above, may be involved in the mechanism for the HF behaviors at low $T$. First, in a local moment model, geometric frustration for AF ordering is present in the V atom substructure which would be expected to suppress static magnetic ordering. Second, the same three $t_{2g}$ orbitals give rise to the combined metallic and local moment behaviors at high $T$ and the HF behaviors at low $T$. This is in strong contrast to $f$-electron HF compounds where the nearly-localized $f$ orbitals are clearly distinguished from the strongly delocalized $s$, $p$ and/or $d$ conduction band states. Third, due to the high symmetry of the V sites, two of the three partially filled $t_{2g}$ orbitals are strictly degenerate from symmetry considerations and are nearly degenerate with the third, so dynamical orbital ordering and the charge degrees of freedom may all be affected by the geometric frustration for AF ordering. This is a complex scenario difficult to treat theoretically.

The physical properties of LiV$_2$O$_4$ are very different from those of LiTi$_2$O$_4$, an isostructural superconductor with a conventional $d$-band $D(E_F)$. The LDA band structures of both compounds are very similar. A successful theoretical framework to explain the low- and high-$T$ physical properties of the $d^{1.5}$ compound LiV$_2$O$_4$ must also be able to explain why these properties are so divergent from those of the $d^{0.5}$ compound LiTi$_2$O$_4$. A beginning has been made by Varma [23] and implicitly as discussed in the previous section. A successful framework will lead to deeper understanding of metallic transition metal oxides generally and perhaps also of the $f$-electron class of heavy fermion compounds.

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[1] G. R. Stewart, Rev. Mod. Phys. 56, 755 (1984); A. C. Hewson, The Kondo Problem to Heavy Fermions (Cambridge University Press, Cambridge, 1993).
[2] M. B. Maple et al., J. Low Temp. Phys. 95, 225 (1994).
[3] S. Kondo, D. C. Johnston, C. A. Swenson, F. Borsa, A. V. Mahajan, L. L. Miller, T. Gu, A. I. Goldman, M. B. Maple, D. A. Gajewski, E. J. Freeman, N. R. Dilley, R. P. Dickey, J. Merrin, K. Kojima, G. M. Luke, Y. J. Uemura, O. Chmaissem, and J. D. Jorgensen, Phys. Rev. Lett. 78, 3729 (1997).
[4] D. B. Rogers, J. L. Gilson, and T. E. Gier, Solid State Commun. 5, 263 (1967).
[5] B. Reuter and J. Jaskowsky, Angew. Chem. 72, 209 (1960); Ber. Bunsen-Ges. Phys. Chem. 70, 189 (1966).
[6] O. Chmaissem, J. D. Jorgensen, S. Kondo, and D. C. Johnston, Phys. Rev. Lett. 79, 4866 (1997).
[7] D. C. Johnston, H. Prakash, W. H. Zachariasen, and R. Viswanathan, Mater. Res. Bull. 8, 777 (1973); D. C. Johnston, J. Low Temp. Phys. 25, 145 (1976).
[8] H. Kessler and M. J. Sienko, J. Chem. Phys. 84, 5414 (2005); see also Y. Nakajima et al., Physica (Amsterdam) 185C-189C, (1991) and Ref. [9].
[9] D. C. Johnston, T. Ami, F. Borsa, M. K. Crawford, J. A. Fernandez-Baca, K. H. Kim, R. L. Harlow, A. V. Mahajan, L. L. Miller, M. A. Subramanian, D. R. Torgeson, and Z. R. Wang, Springer Ser. Solid-State Sci. 119, 241 (1995).
[10] S. Kondo, D. C. Johnston, and L. L. Miller, Phys. Rev. B 59, 2609 (1999).
[11] Y. Ueda, N. Fujisawa, and H. Yasuoka, J. Phys. Soc. Jpn. 66, 778 (1997).
[12] M. Onoda, H. Imai, Y. Amako, and H. Nagaosa, Phys. Rev. B 56, 3760 (1997).
[13] D. C. Johnston, C. A. Swenson, and S. Kondo, Phys. Rev. B 59, 2627 (1999).
[14] H. Takagi et al., unpublished.
[15] N. Fujisawa, Y. Ueda, and H. Yasuoka, Physica B 237-238, 59 (1997); N. Fujisawa, H. Yasuoka, and Y. Ueda, Phys. Rev. B 57, 3539 (1998).
[16] A. V. Mahajan, R. Sala, E. Lee, F. Borsa, S. Kondo, and D. C. Johnston, Phys. Rev. B 57, 8890 (1998).
[17] A. Krabben, A. Loidl, M. Klemm, W. Scharf, and H. Schober, Phys. Rev. Lett. 82, 2919 (1999).
[18] D. C. Johnston, A. Lacerda, S. Kondo, et al., unpublished.
[19] V. Eyert, K.-H. Hock, S. Horn, A. Loidl, and P. S. Ribeiro, Europhys. Lett. 46, 762 (1999).
[20] J. Matsuno, A. Fujimori, and L. F. Mattheiss, Phys. Rev. B 60, 1607 (1999); J. Matsuno, K. Kobayashi, A. Fujimori, L. F. Matheiss, and Y. Ueda, Physica B (to be published).
[21] V. I. Anisimov, M. A. Korotin, M. Zöll, T. Pruschke, K. Le Hur, and T. M. Rice, Phys. Rev. Lett. 83, 364 (1999).
[22] D. J. Singh, P. Blaha, K. Schwarz, and I. I. Mazin, cond-mat/9907206 v2 (unpublished).
[23] C. M. Varma, Phys. Rev. B 60, R6973 (1999).