LiV_2O_4: A Heavy Fermion Transition Metal Oxide

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A crossover with decreasing temperature T from localized moment magnetism to heavy Fermi liquid behavior is reported for the metallic compound LiV_2O_4 with the fcc normal-spinel structure. At $T = 1$ K, the electronic heat capacity coefficient $\gamma \approx 0.42$ J/mol K^2 is exceptionally large for a transition metal compound, the Wilson ratio $\approx$1.7, and the Korringa ratio $\approx$0.7. Our sample with the lowest level of paramagnetic defects showed no static magnetic order above 0.02 K. Superconductivity was not observed above 0.01 K. [S0031-9007(97)03196-7]

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The current interest in highly correlated electron systems has been sparked by several discoveries: These include f-electron intermetallics with heavy Fermi liquid (FL) ground states [heavy fermion (HF) compounds] [1] or non-FL ground states [2], and high-T_c cuprate superconductors. The above HF f-electron compounds (e.g., $CeAl_3$, UPt_3) have enormous electronic heat capacity coefficients $\gamma(T) \equiv C(T)/T \sim 1$ J/mol K^2, where $C(T)$ is the electronic heat capacity, from which quasiparticle effective masses of several hundred times the free electron mass have been inferred. In this Letter, we report the discovery of HF behavior in the transition metal oxide LiV_2O_4. To our knowledge, this is the first report of a d-electron material exhibiting HF behavior characteristic of those of the heaviest-mass f-electron systems. In such systems a high and narrow ($\sim$10 meV) peak occurs at low T in the quasiparticle density of states $\mathcal{D}$ near the Fermi energy E_F, a many-body effect [1]. The large $\mathcal{D}(E_F)$ is reflected in a large, nearly T-independent magnetic spin susceptibility $\chi^{\rm spin}$ and γ compared with the respective 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 (FLs), where $R_W \equiv \pi^2 k_B^2 \chi^{\rm spin}/3\mu_B^2\gamma$, k_B is the Boltzmann's constant, and μ_B is the Bohr magneton. However, at higher T, the $\mathcal{D}(E)$ 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 γ with T, as we observe for LiV_2O_4 above $\sim$4 K, but which is not observed for conventional metals or, to our knowledge, reported for any metallic oxide in which γ is enhanced by proximity to a metal-insulator phase boundary.

LiV_2O_4 is metallic [3] with the fcc normal-spinel structure [4], containing equivalent V ions in slightly distorted octahedral coordination by O. LiV_2O_4 manifestly exhibits strong electron correlations (local moment magnetism). The magnetic susceptibility $\chi(T)$ (4.2–308 K) was found to be the sum of a T-independent term $\chi_0 = 0.4 \times 10^{-4}$ cm^3/mol 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. The negative Weiss temperature $\theta = -63$ K indicates antiferromagnetic (AF) V spin interactions. However, no evidence for magnetic ordering above 4.2 K was found. The local moment behavior contrasts strongly with the relatively T-independent Pauli paramagnetism and superconductivity ($T_c \leq 13.7$ K) of isostructural $LiTi_2O_4$ [6]. Band structure calculations for $LiTi_2O_4$ yield a t_{2g} conduction bandwidth $W \sim 2$ eV [7]. Photoemission measurements on LiV_2O_4 revealed strongly correlated electron behavior with a V intra-atomic Coulomb repulsion parameter $U \sim 2$ eV $\sim W$ [8]. The nature of the ground state is unknown up to now.

We carried out crystallography, electrical resistivity ρ, magnetization M, heat capacity $C_{\rm p}$, ^{7}Li nuclear magnetic resonance NMR and positive-muon spin relaxation (μSR) measurements on LiV_2O_4. We report a crossover with decreasing T from the local moment behavior to heavy FL behavior. We find an enormous $\gamma(1\ {\rm K}) \approx 0.42$ J/mol K^2, much larger than those of other metallic transition metal compounds, e.g., $Y_{1-x}Sc_xMn_2$ ($\lesssim$0.2 J/mol K^2 [9]) and $V_{2-y}O_3$ ($\lesssim$0.07 J/mol K^2 [10]). The magnitudes and T dependences of γ and χ and the T dependence of ρ [3] for LiV_2O_4 are remarkably similar to those of the HF f-electron superconductor UPt_3 ($T_c = 0.54$ K) [1,11,12]. We infer that paramagnetic defects seen in $\chi(T)$ can strongly influence the $C_{\rm p}(T)$ and spin dynamics of LiV_2O_4 below 1 K.

Polycrystalline LiV_2O_4 samples were made using techniques in [6] and were single phase or very nearly so by x-ray and neutron diffraction. Neutron diffraction measurements were carried out at the Intense Pulsed Neutron Source at Argonne National Laboratory. $M(H,T)$ data (H = applied magnetic field) were obtained with SQUID and Faraday magnetometers at Ames and La Jolla, and $C_p(H,T)$ data using heat-pulse calorimeters at Ames and La Jolla. ^{7}Li NMR measurements were done at 17 and 135 MHz with a pulse Fourier transform spectrometer; the recovery of the nuclear magnetization, measured by the echo signal after a saturating radio frequency pulse sequence, was exponential. μSR time spectra in zero and longitudinal H were obtained at TRIUMF.

X-ray and neutron diffraction data on three LiV_2O_4 samples revealed no distortion from the spinel structure (space group $Fd3m$) between 295 and 9 K. Rietveld refinements of the neutron data for sample 5 yielded the lattice and oxygen parameters $a_0 = 8.23932(3)$ Å, $x = 0.26125(2)$ at 295 K, and $a_0 = 8.22694(3)$ Å, $x = 0.26109(2)$ at 12 K. $\rho(T)$ measurements down to 0.01 K showed no evidence for superconductivity.

$\chi(T)$ data from 2 to 400 K are shown for LiV_2O_4 sample 1 in Fig. 1. Above ~50 K, Curie-Weiss-like behavior is seen as previously reported. We assumed that $\chi(T) = \chi_0 + \chi_{\rm loc}^{\rm spin}(T)$, where $\chi_{\rm loc}^{\rm spin}(T)$ was the high-T series expansion to sixth order in $1/T$ of the $S = 1/2$ nearest-neighbor AF Heisenberg model for the V sublattice of the spinel structure [13]. The fit parameters depended on the T region of the fits as previously found assuming $\chi_{\rm loc}^{\rm spin}(T) = C/(T - \theta)$ [14]. Our fit for the range 50–400 K (solid curve in Fig. 1) yielded $\chi_0 = 0.57 \times 10^{-4}$ cm^3/mol, $g = 2.19$, and $\theta = -40$ K, similar to values cited above.

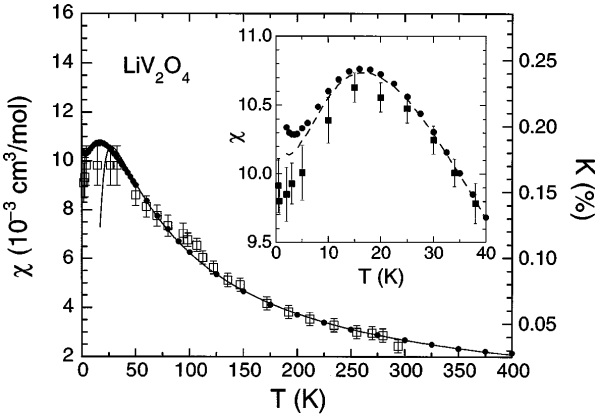

FIG. 1. $\chi \equiv M/H$ ($H = 10$ kG) vs T for LiV_2O_4 sample 1 (•) and ^{7}Li $K(T)$ for sample 2 (□, right-hand scale). The solid curve is a theoretical fit to $\chi(T)$ for $T > 50$ K. The dashed curve and filled squares (inset) denote the intrinsic $\chi(T)$ of LiV_2O_4 inferred from $M(H,T)$ data for samples 1 and 4, respectively (see text).

Contrary to previous reports [5], we find that $\chi(T)$ becomes nearly independent of T below ~30 K, with a shallow broad maximum at ≈16 K (Fig. 1 inset). Field-cooled and zero-field-cooled $M(H = 10\ \text{G}, T)$ data above 2 K showed no evidence for spin-glass ordering. A Curie-like $C_{\rm imp}/T$ upturn in $\chi(T)$ is seen in Fig. 1 below ~5 K, found to be sample dependent. $M(H \le 55\ \text{kG})$ isotherms above 15 K were linear, but at 2 K exhibited negative curvature which increased with increasing $C_{\rm imp}$ in various samples, indicating that this curvature and the Curie term arise from paramagnetic impurities/defects. The $M(H,T)$ data yielded the impurity $S_{\rm imp} \approx 2$ and $g_{\rm imp} \approx 2$, with concentrations 0.03, 0.35, 0.15, 0.08, and 0.70 mol% in samples 1–5, respectively. The intrinsic $\chi(T)$ for LiV_2O_4 inferred by subtracting the impurity contributions in samples 1 and 4 is shown in the inset of Fig. 1, where $\chi(0.4\text{–}2\ \text{K}) = 0.0100(2)$ cm^3/mol.

The ^{7}Li $K(T)$ (Fig. 1) scales approximately linearly with $\chi(T)$ as found above 30 K in [15,16]. $1/T_1(T)$ (Fig. 2) shows an unusual maximum (at 30–50 K), also seen in ^{27}Al $1/T_1(T)$ for the HF compound $CeAl_3$ [17] with $\gamma \sim 1.6$ J/mol K^2 [1], evidently reflecting the crossover from FL (low T) to local moment (high T) behaviors. From the Fig. 2 inset, $1/T_1 \approx (2.4\ \text{sec}^{-1}\,\text{K}^{-1})T$. From Fig. 1, $K(T)$ is nearly constant (≈0.17%) below 30 K. Thus, the Korringa ratio $K^2T_1T/S_{\rm Li}$, where $S_{\rm Li} = 1.74 \times 10^{-6}$ sec K, is constant (≈0.7) below 4 K. These low-T observations are consistent with expectations for a FL. Our 1.6–4.2 K value of ^{7}Li $1/T_1T$ in LiV_2O_4 is a factor of ~6000 greater than that in $LiTi_2O_4$ [18], implying an enhancement of the dressed density of states $\mathcal{D}(E_F)$ by a factor $\sqrt{6000} \sim 80$. However, comparison of this ratio of 80 with the ratio ~20 of the $\gamma(1\ \text{K})$ values for the two compounds (below) suggests a difference in the ^{7}Li hyperfine coupling constants.

$C_p(T)$ data up to 80 K for LiV_2O_4 are shown in Fig. 3(a). Also shown are data for the isostructural nonmagnetic insulator $Li_{4/3}Ti_{5/3}O_4$ obtained to estimate the

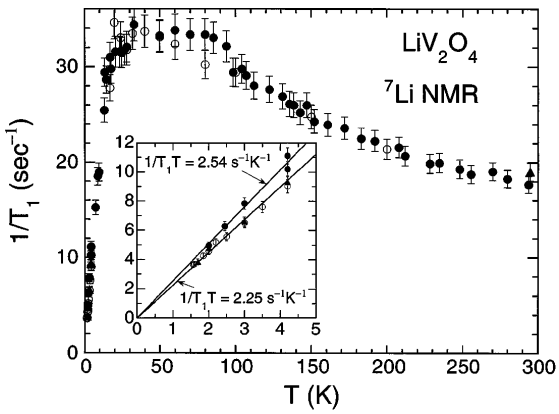

FIG. 2. ^{7}Li $1/T_1$ vs T for LiV_2O_4 samples 1 (filled triangles), 2 (•), and 4 (∘). The lowest-T data are shown in the inset, along with proportional fits.

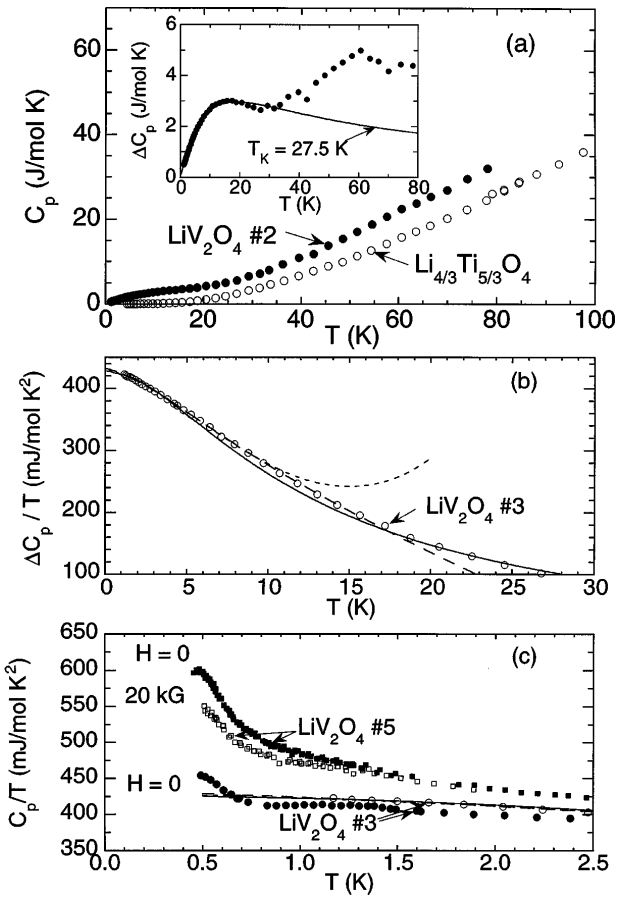

FIG. 3. (a) C_p vs T for LiV_2O_4 sample 2 (•) and $Li_{4/3}Ti_{5/3}O_4$ (∘). Inset: electronic contribution $\Delta C_p(T)$ for sample 2 (•). The solid curve is a 1–5 K fit by Kondo theory. (b) $\Delta C_p(T)/T \equiv \gamma(T)$ for sample 3 below 30 K (∘) (the data for samples 2 and 3 are nearly identical). (c) $\gamma(T \leq 2.5$ K) data for sample 3 from Ames [∘ from (b)] and La Jolla (•), and for sample 5 at $H = 0$ and 20 kG from La Jolla (squares). The curves in (b) and (c) are fits to the Ames data for sample 3 above 1.2 K by theories for Fermi liquids (see text).

lattice contribution. After multiplying the T scale of $C_p(T)$ for $Li_{4/3}Ti_{5/3}O_4$ by 0.941 to take into account the different masses of $Li_{4/3}Ti_{5/3}O_4$ and LiV_2O_4 and subtracting this corrected lattice contribution from the data for LiV_2O_4, the inferred electronic heat capacity $\Delta C_p(T)$ for LiV_2O_4 was obtained (inset). $\Delta C_p(T)$ shows a broad peak near 16 K, and a distinct additional contribution above ~25 K, also seen in $LiTi_2O_4$ [19]. Figure 3(b) shows $\gamma(T) \equiv \Delta C_p(T)/T$ below 30 K, where a strong increase with decreasing T is observed. We obtain $\gamma(1\text{ K}) \approx 0.42$ J/mol K^2, about twenty times larger than in $LiTi_2O_4$ [19]. Using $\chi^{\text{spin}}(1\text{ K}) = 0.01$ cm^3/mol, the Wilson ratio $R_W(1\text{ K}) \approx 1.7$. These low-$T$ results indicate heavy FL behavior [1]. In this interpretation, the nearly T independent $\chi(T)$ and $K(T)$ for $T \lesssim 30$ K in Fig. 1 is a reflection of the disappearance of the V local moments.

$\gamma(T = 1.2$–5 K) for LiV_2O_4 was fitted by the prediction for the $S = 1/2$ Kondo model ($R_W = 2$) [1], yielding a Kondo temperature $T_K = 27.5$ K [solid curves in Figs. 3(a) inset and 3(b)]. This single-parameter fit extrapolated to higher T also describes well the $\Delta C_p(T)$ data up to ~30 K, including the magnitude and temperature of the broad maximum near 16 K [Fig. 3(a) inset]. A 1–10 K fit of $\gamma(T)$ by the FL prediction $\gamma(T) = \gamma(0) + \delta T^2 \ln(T/T_0)$ [1] is shown by the short-dashed curve in Fig. 3(b), for which $\gamma(0) = 428$ mJ/mol K^2, $\delta = 1.6$ mJ/mol K^4, and $T_0 = 25$ K, parameters remarkably similar to those of UPt_3 [11]. $\gamma(T)$ is also consistent with theory [20] for a three-dimensional AF-coupled quantum-disordered FL. A 1–10 K fit by the theory [long-dashed curve in Fig. 3(b)] gave parameters [20] $N = 3$, $\gamma_0 = 810$ mJ/mol K^2, $r = 0.78$, and $T^* = 9.7$ K.

Low-T $\gamma(T)$ data and the above theoretical fits for LiV_2O_4 sample 3 are shown in Fig. 3(c). The data exhibit a plateau with $\gamma \approx 0.42$ J/mol K^2 from ~1.3–0.8 K and an upturn at lower T. The $\gamma(T)$ data in Fig. 3(c) for sample 5, which contains a higher level of magnetic defects (above), increase monotonically down to ≈0.5 K, where the data appear to exhibit a maximum with value ≈0.6 J/mol K^2. Below ~2 K, $\gamma(T, H = 20$ kG) for sample 5 in Fig. 3(c) is suppressed relative to $\gamma(T, H = 0)$. The $H = 0$ results indicate that the presence of magnetic defects increases $C_p(T)$, especially at low T.

Zero-field (ZF) μSR spectra for sample 1 exhibit a single-exponential decay $\exp(-t/T_1)$ (after correction for effects due to nuclear dipolar fields). $1/T_1$ at 20 mK in ZF and in longitudinal field LF = 50 G show little difference (see Fig. 4 inset), indicating that the depolarization is due mostly to fluctuating dynamic local fields. The average fluctuation rate at 20 mK, obtained from the LF dependence, is $\nu \sim \gamma_\mu \times 150\text{ G} \sim 12\ \mu\text{s}^{-1}$, where γ_μ is the positive muon (μ^+) gyromagnetic ratio. The instantaneous random local field H_r inferred from $1/T_1 \sim (\gamma_\mu H_r)^2/\nu$ is then $H_r \sim 30$ G. This H_r is about 50 times smaller than $H_r \sim 1.5$ kG which we observed in the AF state of isostructural ZnV_2O_4, suggesting that H_r in LiV_2O_4 sample 1 is due to dilute (% level) paramagnetic impurities. The $1/T_1(T)$ in Fig. 4 indicates a slowing down of impurity spin fluctuations with decreasing T, yet we found no signature of static spin freezing in sample 1 down to 20 mK. In contrast, the ZF-μSR spectra in sample 3 (with a larger Curie term in χ) showed two-component relaxation below $T \sim 0.8$ K, with a fast 2/3 component and slow 1/3 component, characteristic of static spin freezing. This behavior correlates with the C_p anomaly at $T \sim 0.8$ K observed for sample 3 in Fig. 3(c). Unfortunately, $1/T_1$ for μ^+ due to itinerant HF quasiparticles, as inferred from NMR in Fig. 2, is not clearly visible in Fig. 4, overshadowed by the depolarization due to fluctuating/freezing local fields. However, this is not surprising in view of the unobservably small $1/T_1$ for μ^+ in the HF compounds UPt_3 [21] and UBe_{13}.

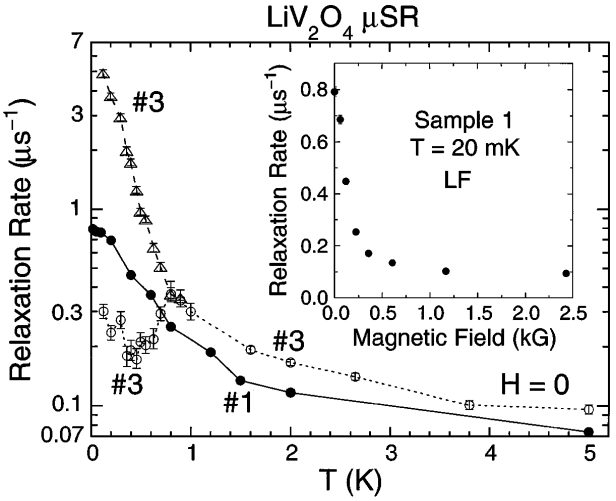

FIG. 4. μSR rate in LiV_2O_4 obtained in $H = 0$ vs T (main figure) and vs longitudinal field (LF) at $T = 20$ mK (inset). Rates for sample 1 at all T and LF ($\bullet$) and sample 3 for $T \gtrsim 0.8$ K ($\circ$) represent $1/T_1$ in fits of the μSR time t spectra by $\exp(-t/T_1)$, while two rates for sample 3 for $T \lesssim 0.8$ K represent $1/T_2$ ($\triangle$) and $1/T_1$ ($\circ$) in fits by $0.67\exp(-t/T_2) + 0.33\exp(-t/T_1)$.

In conclusion, our $\chi(T)$, $C_p(T)$, and ^{7}Li NMR measurements on LiV_2O_4 demonstrate a crossover with decreasing T from localized moment to heavy FL behavior, with a Kondo or spin-fluctuation temperature $T_K \sim 28$ K. The $\rho(T)$ data show a pronounced smooth downturn below $\sim$30 K [3], consistent with Kondo lattice behavior in which the onset of electronic coherence below T_K reduces ρ [1]. $\rho(T)$ data on single crystals at low $T \lesssim 4$ K are needed to test whether a T^2 temperature dependence is observed as expected for a FL. The geometric frustration for AF ordering inherent in the V sublattice of the spinel structure may help to destabilize the local moments in LiV_2O_4 at low T [9] and lead to the FL behavior.

Note added.—Ueda *et al.* and Fujiwara *et al.*, respectively, have independently obtained $\chi(T)$ and ^{7}Li NMR data on LiV_2O_4 [22] similar to ours.

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