LiV$_2$O$_4$ Spinel as a Heavy-Mass Fermi Liquid: Anomalous Transport and Role of Geometrical Frustration

C. Urano,[1] M. Nohara,[1] S. Kondo,[1] F. Sakai,[2] H. Takagi,[1,3] T. Shiraki,[4] and T. Okubo[4]

[1]*Department of Advanced Materials Science and Department of Superconductivity, University of Tokyo, Hongo, Bunkyo-ku, Tokyo 113-8656, Japan*

[2]*Institute for Solid State Physics, University of Tokyo, Kashiwanoha, Kashiwa-shi, Chiba 277-8581, Japan*

[3]*CREST, Japan Science and Technology Corporation, Japan*

[4]*Department of Chemical System Engineering, University of Tokyo, Hongo, Bunkyo-ku, Tokyo 113-8656, Japan*

Transport and specific heat measurements on hydrothermally grown single crystals reveal the formation of a heavy-mass Fermi liquid in the LiV$_2$O$_4$ spinel, below a coherence temperature of $T^* = 20-30$ K. A few observations which illustrate the uniqueness of this spinel are discussed in connection with the origin of the heavy mass, such as the anomalous absence of resistivity saturation above T^* and the close proximity to a spin glass phase where the influence of the magnetic frustration is evident.

Among the variety of structural categories of oxides, the spinel, generally denoted by the chemical formula AB$_2$O$_4$, has been one of the most familiar structures along with the well-known perovskite. The spinel structure consists of two basic units, AO$_4$ tetrahedron and BO$_6$ octahedron. The latter is connected with each other by the edges. One of the unique features of the spinel structure is that the B ions form a sublattice of corner-shared tetrahedra. When the B cations are magnetic and the magnetic coupling between them is antiferromagnetic (AF), this lattice gives rise to a strong magnetic frustration [1]. Therefore, if a metallic spinel is located in the vicinity of a correlation-driven metal-insulator transition, a novel interplay between the charge carriers and the frustrated spin degree of freedom might be expected. Most spinel oxides, however, are known to be insulating and, to date, only two spinel oxides, LiTi$_2$O$_4$ and LiV$_2$O$_4$, have been reported to be conducting. LiTi$_2$O$_4$ is a well-known BCS superconductor with a transition temperature $T_c = 13.7$ K [2].

In LiV$_2$O$_4$, the formal oxidation state of the V ion is 3.5+ and consequently, almost triply degenerate t_{2g} orbitals in the nearly cubic crystal field accommodate 1.5 electrons per V ion. LiV$_2$O$_4$ remains cubic down to low T [3] and no magnetic ordering occurs above 20 mK [4,5], indicating that all V sites are crystallographically equivalent. Therefore, if the material is clean enough, a metallic ground state is expected. Recently, Kondo, Johnston, and co-workers measured specific heat $C(T)$ and magnetic susceptibility $\chi(T)$ on polycrystalline LiV$_2$O$_4$ samples [6–8]. They found an extremely large quasiparticle specific heat coefficient $\gamma \sim 420$ mJ/mol K^2, comparable to that of the heavy fermion intermetallic UPt$_3$ [9]. Combining the γ and the $T = 0$ limit $\chi(0)$, a Wilson ratio, $R_W = 1.7$, was obtained which is reasonable for a strongly correlated Fermi liquid. From these results, Kondo *et al.* concluded that LiV$_2$O$_4$ is the first heavy fermion transition metal oxide. Since it contains only d electrons,

the origin of the large γ has been a subject of ongoing debate.

Since the very early single crystal study performed more than three decades ago [10], all works on this intriguing compound had been performed using ceramic samples, including the pioneering work of Kondo *et al.* To our knowledge, however, the resistivity $\rho(T)$ of all polycrystalline LiV$_2$O$_4$ reported thus far exhibits insulating behavior and tends to diverge towards the $T = 0$ limit [11,12], while metallic behavior was reported by the early single crystal study [10]. It is not clear whether this metallic single crystal yields a large γ as observed in ceramic samples. Besides, low-T transport measurements have not yet been performed on single crystalline samples [10].

With these features in mind, we have grown single crystals of LiV$_2$O$_4$ and have measured their transport properties, magnetization, and specific heat. In this Letter, we first present evidences, mainly from the low-T transport properties, that the ground state of LiV$_2$O$_4$ is indeed an extraordinarily heavy-mass Fermi liquid [13]. We then address a few basic issues such as the high-T incoherent transport behavior and a role of geometric frustration, which, we believe, is closely linked with the origin of the heavy quasiparticle mass.

Single crystals of LiV$_2$O$_4$ were grown by a hydrothermal technique [10]. No evidence for cation nonstoichiometry was found by inductively coupled plasma analysis within a given resolution (1%). Polycrystalline samples of Li$_x$Zn$_{1-x}$V$_2$O$_4$ were prepared by a conventional solid state reaction [14]. The T-dependent resistivity was measured by a four-probe technique with an ac resistance bridge. A thermal relaxation calorimeter was used to measure the $C(T)$ of tiny single crystalline samples, while an adiabatic calorimeter was used for the polycrystalline samples.

Figure 1 summarizes all the physical properties we have measured on single crystals. As clearly seen in Fig. 1(a), $\rho(T)$ of the single crystal is metallic down to 300 mK, in
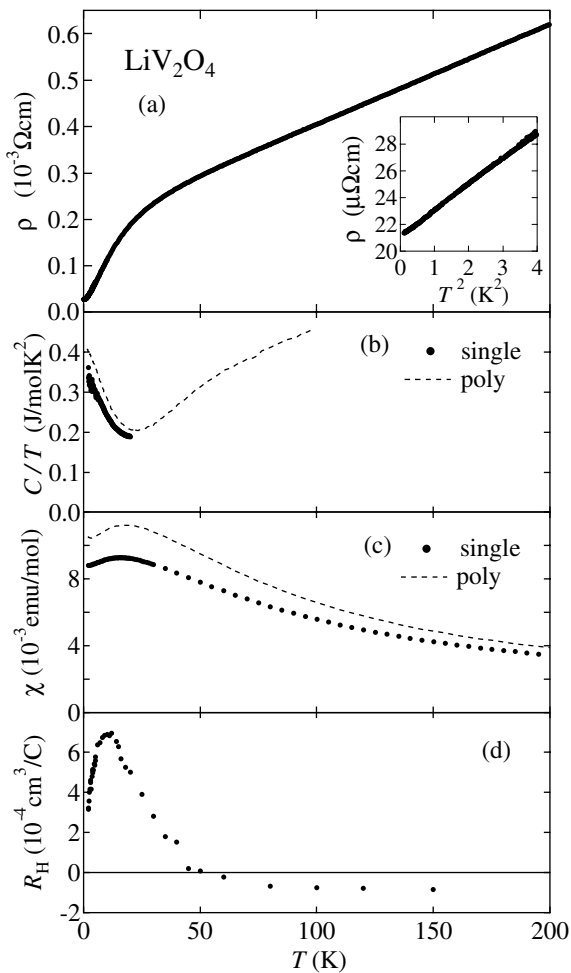
FIG. 1. T dependence of various physical properties of LiV_2O_4 single crystal. (a) Resistivity ρ, (b) specific heat C divided by T, (c) magnetic susceptibility χ, and (d) Hall coefficient R_H. C/T and χ data for polycrystalline LiV_2O_4 are shown for comparison in (b) and (c), respectively. In the inset of (a), ρ of LiV_2O_4 below 2 K is plotted against T^2.

marked contrast with the polycrystalline results [11,12]. Nevertheless, in $C(T)/T$ and $\chi(T)$, shown in Figs. 1(b) and 1(c), the polycrystalline results by Kondo *et al.* were essentially reproduced. $C(T)/T$ shows a noticeable increase below around 30 K and an extrapolation to $T = 0$ yields $\gamma \sim 350$ mJ/mol K^2. Although this is about 15% smaller than observed in polycrystalline samples, most likely due to a subtle difference in the sample quality, it is still true that the observed γ is extraordinarily large. $\chi(T)$ [15] shows Curie-Weiss behavior at high T, with a shallow and broad peak around 16 K. The Curie-Weiss fitting of $\chi(T)$ in the T range $100 \leq T \leq 300$ K gives a Curie constant $C_{Curie} = 0.34$ cm^3 K/V mol, which corresponds to a $S = 1/2$ moment per V ion, and a Curie-Weiss constant $\Theta_{CW} = -37$ K (AF). Combining the γ and $\chi(0) = 0.88 \times 10^{-2}$ cm^3/mol at the $T = 0$ limit, a reasonable Wilson ratio of $R_W = 1.8$ was obtained, in agreement with Refs. [6–8].

A further crucial test for the appearance of a heavy-mass Fermi liquid ground state is the observation of a T^2 behavior in $\rho(T)$, which is closely linked with the ω^2 dependence of the inverse quasiparticle lifetime. In the inset of Fig. 1(a), we show clearly that $\rho(T)$ indeed follows T^2 behavior below 2 K, indicative of a Fermi liquid ground state. Other possible power laws, such as $T^{1.5}$ expected for the AF critical point, were also examined. However, it turned out that T^2 best describes the T dependence below 2 K. The coefficient of the T^2 term $A = 2.0 \mu\Omega$ cm/K^2 is extremely large, consistent with the extraordinary large γ. Indeed, the observed γ and A roughly satisfy the Kadowaki-Woods relation [16], $A/\gamma^2 \sim 10^{-5} \mu\Omega$ cm/ K^2/(mJ/mol K^{-2})^2, which is known to hold for a variety of strongly correlated Fermi liquids.

As pointed out in previous polycrystalline studies [6–8], an increase of $C(T)/T$ and a deviation of $\chi(T)$ from the Curie-Weiss behavior upon lowering T become apparent around 20–30 K. In accord with these changes in $C(T)/T$ and $\chi(T)$, the transport properties also show a noticeable change around the same T range, supporting the existence of a coherence temperature, T^*, below which the coherent heavy-mass quasiparticle states are formed, analogous with the dense Kondo systems. In $\rho(T)$ shown in Fig. 1(a), a pronounced kneelike structure is clearly observed around 30 K, below which $\rho(T)$ shows a rapid decrease towards the low temperature T^2 behavior with decreasing T. The Hall coefficient $R_H(T)$, measured under 1.4 T and shown in Fig. 1(d), is negative in sign and almost T independent at high T. On decreasing T, however, $R_H(T)$ changes sign around 50 K and develops a strong T dependence with a pronounced peak below about 30 K. It is noted that this behavior is surprisingly similar to that typically observed in heavy fermion intermetallics below their coherence temperature [17].

It is now clear from these results that a heavy-mass Fermi liquid ground state, with a coherence temperature T^* of 20–30 K, is realized in LiV_2O_4. The low-T properties (i.e., below T^*) are strikingly similar to those of intermetallic dense Kondo systems. Unlike dense Kondo systems, however, it is not obvious to identify two distinct subsystems, conduction electrons and localized moments in these spinel compounds. Recent local density approximation (LDA) band calculations indeed indicate that the conduction bands, with width 2 eV, are made up almost entirely of V t_{2g} character. In this context it was pointed out that the observed heavy quasiparticle mass should be attributed to some non-Kondo mechanism, for example, strong AF spin fluctuations due to geometrical frustration [18,19]. Anisimov *et al.*, in contrast, argued that this system can be mapped onto a dense Kondo system [20]. Because of a small trigonal distortion of the VO_6 octahedron, the V t_{2g} orbitals split into an A_{1g} orbital and doubly degenerate E_g orbitals, which are more itinerant in character than the A_{1g} orbital. In their scenario based on LDA $+$ U calculation, among the 1.5 electrons in V t_{2g} orbital, 0.5

electron enters into the broad E_g bands and one electron occupies the lower Hubbard band of the highly localized A_{1g} band, giving rise to itinerant carriers and localized $S = 1/2$ moments, respectively.

In view of our yet incomplete understanding of the origin of the heavy quasiparticle mass, it may be informative to address a few basic questions. An obvious question is whether there is any evidence for Kondo scattering above T^*. $\rho(T)$ extended up to 700 K is displayed in Fig. 2 [21]. Above $T^* = 20–30$ K, we do not see the $\log T$ dependence normally associated with Kondo scattering. Instead, $\rho(T)$ shows a *steep increase* with increasing T without any trace of saturation. The magnitude of $\rho(T)$ is unusually high for a metal, of the order of a few mΩ cm above room temperature. This is again in marked contrast to the behavior found in dense Kondo systems, where the magnitude of the resistivity above the coherence temperature is usually ~ 100 $\mu\Omega$ cm (see Fig. 2). The large $\rho(T)$ value here yields unreasonably small estimates for the electron mean free path, smaller than the nearest neighbor V-V distance, in fact. At 500 K, for example, a free electron estimate with a carrier density of 1.5 and 0.5 per V gives a mean free path of 0.71 and 1.47 Å, respectively. These should be compared with the nearest V-V distance of 2.91 Å [3]. Therefore, at first glance, the "metallic" behavior above T^* does appear in fact to be highly incoherent in nature. It may be interesting to infer that quite similar behavior, i.e., a steep increase in $\rho(T)$ far beyond the Ioffe-Regel limit, is generally observed in metals located near a Mott transition, such as V_2O_3 [22] and $NiS_{2-x}Se_x$ [23], where $\rho(T)$ crosses over to a high-T insulating phase.

Finally, we would like to address the possible role of the geometric frustration inherent to the cubic spinel structure. In this context, we would like to emphasize that, in the phase diagram of $Li_xZn_{1-x}V_2O_4$ solid solution (see the

inset of Fig. 3), LiV_2O_4 is located right next to the spin glass (SG) phase, where the vital role of the geometrical frustration is evident. ZnV_2O_4, the other end member in this solid solution, is an $S = 1$ Mott insulator with two t_{2g} electrons per V. An unusually low AF ordering temperature, $T_N = 37$ K, contrasting with the large $|\Theta_{CW}|$ of 700 K, estimated from the high-T $\chi(T)$ [24], clearly indicates a substantial influence of the geometrical frustration in ZnV_2O_4. This AF ordering appears to be marginally achieved by experiencing a structural phase transition from cubic to tetragonal [14], which partially relieves the frustration by lifting the orbital degeneracy.

As clearly seen from the phase diagram in the inset of Fig. 3, the structural phase transition and simultaneously the AF transition are rapidly suppressed by Li doping for Zn and eventually disappear at $x = 0.1$. To quench the unfrozen spin and possibly orbital degrees of freedom, above $x = 0.1$ a SG phase alternatively shows up at low T over a wide composition range. The vital role of the geometrical frustration in this phase is evidenced by the unusual behavior of $C(T)$ in $Li_xZn_{1-x}V_2O_4$ shown in the top panel of Fig. 3. In the SG phase, as previously reported by Ueda *et al.* [14], conventional SG behavior with hysteresis in $\chi(T)$ below the SG transition temperature T_{SG} is observed. The $C(T)/T$ data for the SG phase samples in Fig. 3,
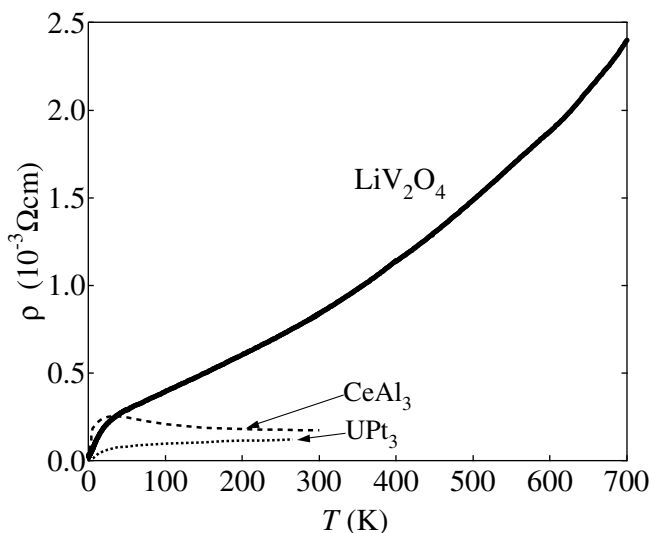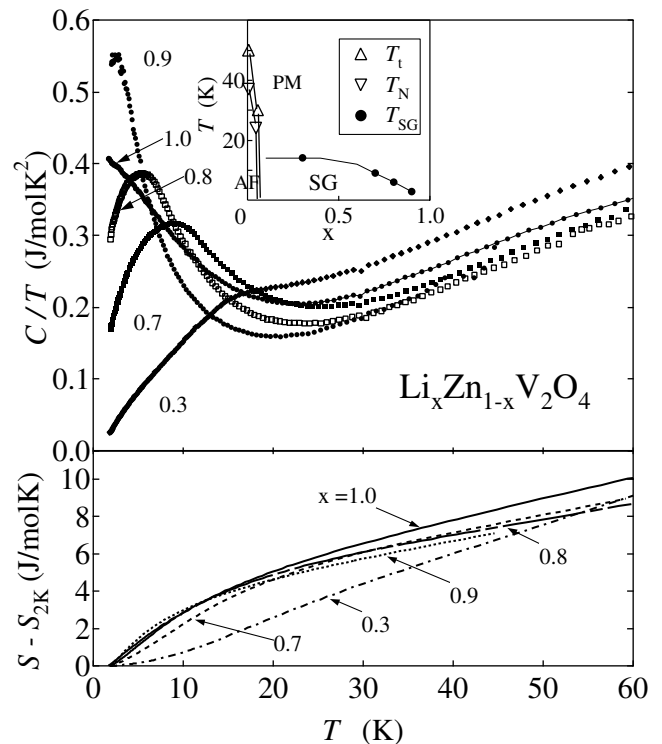

FIG. 2. $\rho(T)$ of LiV_2O_4 up to 700 K is shown. To illustrate the marked contrast to conventional heavy fermion compounds, $\rho(T)$ of $CeAl_3$ and UPt_3, taken from Ref. [17], are also plotted.

FIG. 3. The systematic evolution of $C(T)/T$ of polycrystalline $Li_xZn_{1-x}V_2O_4$ as a function of T for different compositions (upper panel). The magnetic phase diagram of the solid solution is shown in the inset of the upper panel. AF, PM, and SG stand for antiferromagnetic, paramagnetic, and spin glass phases, respectively. ($\triangle$) stands for structural phase transition. The lower panel shows the electronic entropy calculated from C/T.

however, show a distinctly different behavior from those of conventional SG systems, where $C(T)/T$ normally shows a vanishingly small anomaly at T_{SG}, followed by essentially T-independent behavior at low T. By contrast, $C(T)/T$ of Li doped ZnV_2O_4 shows a pronounced peak at T_{SG} and then shows a rapid and almost T-linear decrease below T_{SG}. This unusual behavior is remarkably analogous to those of geometrically frustrated spin systems such as kagomé lattice [25] and, therefore, very likely signals the dominant role of geometrical frustration in the SG phase.

With further Li doping, the SG phase finally vanishes around $x = 1.0$ and the heavy-mass Fermi liquid phase is simultaneously realized. We therefore suspect that the geometrical frustration may play a certain role in realizing the heavy-mass Fermi liquid. It may be interesting to point out that the electronic entropy $S(T)$, shown in the bottom panel of Fig. 3 and estimated from the C/T vs T curve [26], is almost independent of Zn content above T_{SG} and reaches, for example, as large as 50%–60% of $R \ln2/V$ at 50 K. With decreasing T, $S(T)$ is first quenched gradually in the SG compositions, due most likely to the geometrical frustration, then rapidly quenched around T_{SG}. At $x = 1.0$, the SG transition is completely suppressed and the gradual quenching of the residual $S(T)$ continues to the $T = 0$ limit. Apparently, this leads to an extraordinarily large γ in LiV_2O_4.

In summary, from the transport and specific heat measurements on single crystals we have shown strong evidence for the formation of a heavy-mass Fermi liquid in the LiV_2O_4 spinel with a coherence temperature of 30 K. The low temperature transport properties are found to be remarkably similar to those of heavy fermion intermetallics. Nevertheless, the microscopic analogy with heavy fermion intermetallics is not obvious. The high temperature transport behavior, indeed, is substantially different from that observed in heavy fermion intermetallics, for example. It is hard to imagine that the close proximity to the spin glass phase, where the vital role of magnetic frustration is clearly evident, is accidental. These features suggest that a dense Kondo scenario, at least in its simplest form, is not enough to account for the origin of the heavy mass. The question whether or not it requires a mechanism essentially different from the conventional Kondo scenario is worthy of further exploration.

[1] P. W. Anderson, Phys. Rev. **102**, 1008 (1956).

[2] D. C. Johnston, J. Low Temp. Phys. **25**, 145 (1976).

[3] O. Chmaissem et al., Phys. Rev. Lett. **79**, 4866 (1997).

[4] A. V. Mahajan et al., Phys. Rev. B **57**, 8890 (1998).

[5] J. Merrin et al., J. Magn. Magn. Mater. **177**, 799 (1998).

[6] S. Kondo et al., Phys. Rev. Lett. **78**, 3729 (1997).

[7] S. Kondo, D. C. Johnston, and L. L. Miller, Phys. Rev. B **59**, 2609 (1999).

[8] D. C. Johnston, C. A. Swenson, and S. Kondo, Phys. Rev. B **59**, 2627 (1999).

[9] G. R. Stewart et al., Phys. Rev. Lett. **52**, 679 (1984).

[10] D. B. Rogers, J. L. Gillson, and T. E. Gier, Solid State Commun. **5**, 263 (1967).

[11] M. Onoda et al., Phys. Rev. B **56**, 3760 (1997); K. Kawakami, Y. Sakai, and N. Tsuda, J. Phys. Soc. Jpn. **55**, 3174 (1986); Y. Nakajima et al., Physica (Amsterdam) **185C–189C**, 719 (1991).

[12] T. Hayakawa, D. Shimada, and N. Tsuda, J. Phys. Soc. Jpn. **58**, 2867 (1989).

[13] Early confirmation of the metallic ground state based on single crystalline data was presented in H. Takagi et al., Mater. Sci. Eng. B **63**, 147 (1999).

[14] Y. Ueda, N. Fujiwara, and H. Yasuoka, J. Phys. Soc. Jpn. **66**, 778 (1997).

[15] A Curie tail due to magnetic impurities was subtracted. The impurity spin S and their concentration N_{imp}, obtained from the magnetization curves, were $S = 5/2$ and $N_{imp} = 0.16\%$, respectively.

[16] K. Kadowaki and S. B. Woods, Solid State Commun. **58**, 507 (1986).

[17] For reviews, see, e.g., G. R. Stewart, Rev. Mod. Phys. **56**, 755 (1984); Z. Fisk et al., Science **239**, 33 (1988); A. C. Hewson, The Kondo Problem to Heavy Fermions (Cambridge University Press, Cambridge, England, 1993).

[18] V. Eyert et al., Europhys. Lett. **46**, 762 (1999).

[19] J. Matsuno, A. Fujimori, and L. F. Mattheiss, Phys. Rev. B **60**, 1607 (1999).

[20] V. I. Anisimov et al., Phys. Rev. Lett. **83**, 364 (1999).

[21] The measurements were performed in an inert Ar gas flow and no hysteresis was observed between the measurements on increasing and decreasing T, indicating that no chemical change took place during the measurement.

[22] H. Kuwamoto, J. M. Honig, and J. Appel, Phys. Rev. B **22**, 2626 (1980).

[23] R. J. Bouchard et al., Mater. Res. Bull. **8**, 489 (1973).

[24] H. Mamiya and M. Onoda, Solid State Commun. **95**, 217 (1995).

[25] A. P. Ramirez, G. P. Espinosa, and A. S. Cooper, Phys. Rev. Lett. **64**, 2070 (1990).

[26] The lattice contribution to the specific heat was subtracted using that of $LiTi_2O_4$ [8].