From the Geometrically Frustrated Antiferromagnets ZnV_2O_4 and $ZnCr_2O_4$ to the Heavy-Mass Fermi Liquid LiV_2O_4

Shinichiro KONDO,[1] Chiharu URANO,[1] Yusuke KURIHARA,[1] Minoru NOHARA,[1,2] and Hidenori TAKAGI[1,2]

[1]*Department of Advanced Materials Science, Graduate School of Frontier Sciences, the University of Tokyo, 7-3-1 Hongo, Bunkyo-ku, Tokyo 113-8656, Japan*
[2]*CREST, Japan Science and Technology Corporation, Japan*

The specific heat measurements on the geometrically frustrated magnets ZnV_2O_4 and $ZnCr_2O_4$ were carried out. In both compounds, the strong influence of geometric frustration is clearly seen from the large size of residual entropy for the temperature much lower than the corresponding Weiss temperature. Comparing with the result of the chromate which has no orbital degree of freedom, we claim that in ZnV_2O_4 the spin degree of freedom dominates the observed residual entropy. The systematic study of specific heat on the series $Li_xZn_{1-x}V_2O_4$ enables us to identify the dominating role of frustration with the observed, different phases from the Zn end frustrated magnet to the heavy-mass Fermi liquid LiV_2O_4.

KEYWORDS: Geometric frustration, Strongly correlated materials, Heavy fermion

§1. Introduction

Along with the perovskites, the spinel structure is one of the most frequently encountered crystal systems in materials science.[1] Many spinel oxides have been known to manifest interesting physical properties. For example, among many ferrites, magnetite (Fe_3O_4) in particular has drawn so much attention by its still-unsolved problem of Verwey transition.[2] While almost all spinel oxides are insulating, only $LiTi_2O_4$[3] and LiV_2O_4[4] are known to be metallic to low temperatures T. The metallicity of these two compounds can be understood by two reasons: first, the Ti or V cation has only one crystallographically equivalent site; second, the formal oxidation state of Ti or V is non-integral (3.5+/Ti or V).

With the difference of only one electron per transition metal cation (*i.e.* $d^{0.5}$/Ti *vs.* $d^{1.5}$/V), the observed physics of $LiTi_2O_4$ and LiV_2O_4 especially at low T is distinctly different. $LiTi_2O_4$ is a BCS superconductor with the transition temperature $T_c = 13.7\,\text{K}$ and is a simple Pauli paramagnet for $T > T_c$. In contrast, LiV_2O_4 exhibits local magnetic moment behavior but without a long range magnetic ordering to $20\,\text{mK}$.[5-7] LiV_2O_4 was studied by several groups more than a decade ago.[8] However, recently it regains wide attention in physics community. This is because LiV_2O_4 was reported to be the first heavy-fermion (HF) transition-metal oxide.[5] The observed electronic specific coefficient $\gamma = 420\,\text{mJ/mol\,K}^2$ is unprecedentedly large as a transition metal compound and exceeds the previous largest γ values of $(Y, Sc)Mn_2$.[9] Using single crystals of LiV_2O_4, we have recently reported the first transport results at low T. We confirmed the Fermi liquid behavior with heavy quasiparticle mass by observing below $\approx 2\,\text{K}$ the T^2 dependence of electronic resistivity $\rho(T)$ with a large coefficient of the T^2 term, A.[10,11]

In the spinel structure, antiferromagnetically-coupled spins are under geometric frustration.[12] Our naive expectation is then that the heavy mass observed in LiV_2O_4 might have an intimate connection with the frustration. Before pursuing the Fermi liquid LiV_2O_4 further, we focus on its parent insulating compound ZnV_2O_4, and examine the effect of frustration through specific heat $C(T)$ measurements. However, there is a subtlety on our attempt; the orbital degree of freedom might make additional contribution to the observed entropy of ZnV_2O_4 (owing to 2 electrons/V in t_{2g} orbitals under the nearly cubic local field). Thus, in order to experimentally distinguish the roles of spin and orbital in ZnV_2O_4, the other Mott insulator $ZnCr_2O_4$ is utilized as a reference material. The chromate has no orbital degree of freedom left with three electrons in the t_{2g} orbitals. Furthermore, the substitution of Zn in the parent compound with Li makes it possible to carry out the systematic specific heat measurements on the whole series, and to study how the influence of geometric frustration, seen at the Zn-end parent compound, is evolved toward the Li end.

§2. Review of experimental results on single crystal LiV_2O_4

In this first section, the experimental review of the heavy-mass Fermi liquid LiV_2O_4 is given through our results on hydrothermally-grown single crystals. All the physical properties we measured are summarized in Fig. 1. Both $C(T)$ and magnetic susceptibility $\chi(T)$ measurements reproduce polycrystalline results.[5,13,14] $C(T)/T$ exhibits the strong T dependence below about $30\,\text{K}$. The $T = 0$ intercept yields an enormously large value of $\gamma = 350\,\text{mJ/mol\,K}^2$ (Ref. [15]), which is slightly smaller than the polycrystalline value. In the T range 100–$300\,\text{K}$ $\chi(T)$ follows the Curie-Weiss (CW) law[16]

with the Curie constant corresponding to $S = 1/2$ per V and the antiferromagnetic (AF) Weiss temperature of $\theta = 37$ K. $\chi(T)$ begins to deviate from the CW dependence at about 30 K and becomes nearly T independent at lower T with a broad peak at ≈ 16 K. Spin glass behavior was not found in zero-field-cooled (ZFC) and field-cooled (FC) magnetization measurements under low magnetic fields H. The Wilson ratio R_W of 1.8 is obtained, which is reasonable as a strongly correlated Fermi liquid.
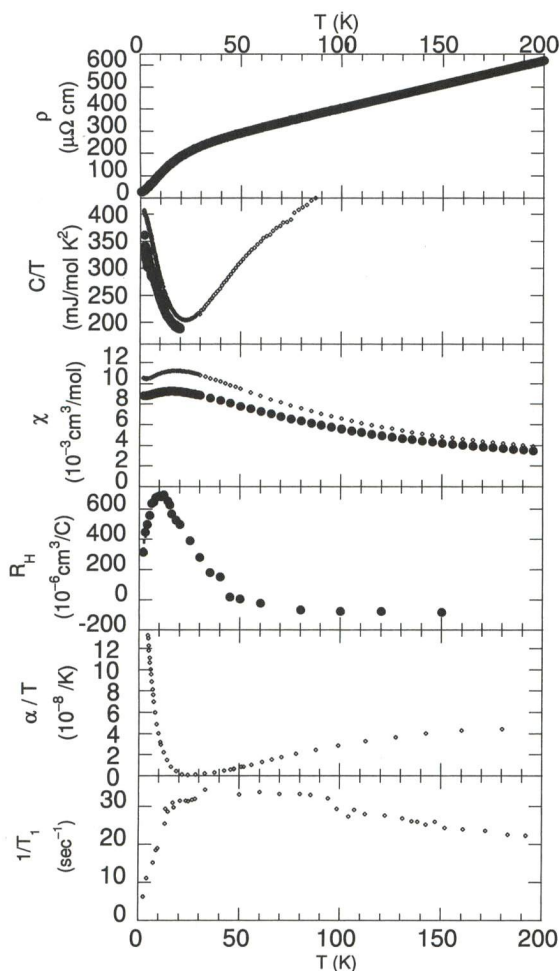
so that with the large γ, LiV$_2$O$_4$ roughly satisfies the Kadowaki-Woods relation[17] like many other strongly correlated compounds including conventional HF systems. The Hall coefficient $R_H(T)$, measured on a single crystal under $H = 1.4$ T, starts to display a pronounced T dependence below ~ 30 K. $R_H(T)$ is nearly T independent in the higher T region. On decreasing T, $R_H(T)$ switches the sign from negative to positive at ~ 40 K and shows a peak around 10 K.
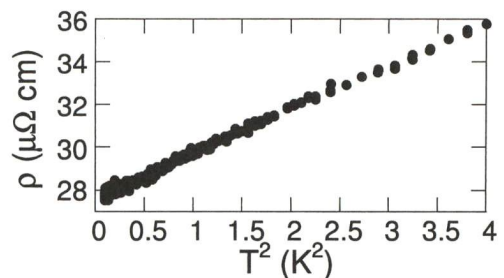

Fig. 2. Low T resistivity $\rho(T)$ of single crystal LiV$_2$O$_4$, plotted against T^2.

From these results shown in Fig. 1, we concluded that there is a characteristic temperature T^* of ~ 30 K, below which a Fermi liquid with the extremely heavy mass starts to form. The low-T behaviors of this $3d$ system are phenomenologically very similar to conventional f electron HF systems.

§3. ZnV$_2$O$_4$, the parent compound of LiV$_2$O$_4$: roles of spin and orbital degrees of freedom

In this section, we study the parent compound of LiV$_2$O$_4$, the $S = 1$ Mott insulator ZnV$_2$O$_4$, anticipating to observe some symptom of the anomalies seen in LiV$_2$O$_4$.

3.1 Review of previous studies

The effect of strong geometric frustration in ZnV$_2$O$_4$ may be inferred from the past work that the AF ordering temperature $T_N \approx 40$ K[18,19] is much lower than the Weiss temperature $\theta = 420$ K.[20] At room temperature, ZnV$_2$O$_4$ has the cubic spinel structure, and transforms into the tetragonal phase $(I4_1/amd)$[21] at the structural phase transition temperature $T_{st} = 50$ K. The AF long-range ordering at 40 K is, therefore, taken place under the tetragonal overall symmetry. In the tetragonal phase $(c/a < 1)$[18] the VO$_6$ octahedron shrinks along c axis and is broadened in ab plane.[21] Under such circumstance, the t_{2g} orbitals split themselves into the singlet d_{xy} at lower energy and the doublet d_{yz} and d_{zx} at higher energy by Jahn-Teller effect, as considered in Ref. [22]. Having one of the 2 electrons/V in the original t_{2g} orbitals into the singlet d_{xy} in the tetragonal phase, the exchange interactions among the V cations along $\langle 110 \rangle$ directions are enhanced.[22] Consequently, geometric frustration is weakened, leading the spin to order. This explains the simple quasi-1-dimensional magnetic structure along $\langle 110 \rangle$ directions found in neutron scattering exper-

Fig. 1. Summary of various measurement results on LiV$_2$O$_4$: (from top) resistivity $\rho(T)$, specific heat $C(T)$ divided by T, magnetic susceptibility $\chi(T)$, Hall coefficient $R_H(T)$, linear thermal expansion coefficient $\alpha(T)$ divided by T (data from Ref. [14]) and spin-lattice relaxation rate $1/T_1$ of ^{7}Li NMR (data from Ref. [7]). Solid circles are single crystal data, while diamonds are polycrystalline results. Note that there is a characteristic temperature ~ 30 K from all the measurements.

$\rho(T)$ of single crystals monotonically decreases as T is lowered. This metallic T dependence is in marked contrast to the insulating behavior of polycrystalline samples. Below ~ 30 K $\rho(T)$ decreases more rapidly. More importantly, for the first time we reported the T^2 dependence of $\rho(T)$ at low $T < 2$ K.[10,11] This is a characteristic T dependence of Fermi liquid and can be readily identified in Fig. 2. In addition, the coefficient of the T^2 term in $\rho(T)$, $A = 2.2$ $\mu\Omega$ cm/K^2, is extremely large,

iments.[18]

The reference compound $ZnCr_2O_4$ is an ideal system to study the spin without being hindered by the other degrees of freedom. Like ZnV_2O_4, the chromate displays both AF and structural phase transitions. However, unlike the vanadate, these two transitions occur at the same temperature, i.e. $T_N = T_{st} \approx 10\,K$.[23–25] Note that strong frustration can be seen from the small ratio of T_N/θ when $\theta = 350\,K$ (Ref. [24]) is used. Jahn-Teller effect cannot be responsible for the structural transition in the chromate. Rather, it is considered that frustrated spins win the competition against the lattice rigidity, achieving lowering of the total energy.[25] The resultant magnetic structure in the ordered state (where $c/a < 1$)[25] is non-collinear,[26,27] much different from that of ZnV_2O_4.

3.2 Specific heat measurement results and discussion

From our specific heat measurement results on ZnV_2O_4 as well as $ZnCr_2O_4$ we find the further evidence for the strong influence of geometric frustration. $C(T)$ of polycrystalline ZnV_2O_4 and $ZnCr_2O_4$ samples prepared by ordinary solid-state technique was measured in an adiabatic calorimeter. After the subtraction of lattice contribution,[28] the remaining "electronic" specific heat is plotted as a $C_{el}(T)/T$ vs. T in Figs. 3 and 4. By integrating the area under the $C_{el}(T)/T$ curve, the electronic entropy $S_{el}(T)$ is calculated to the respective lowest temperatures.
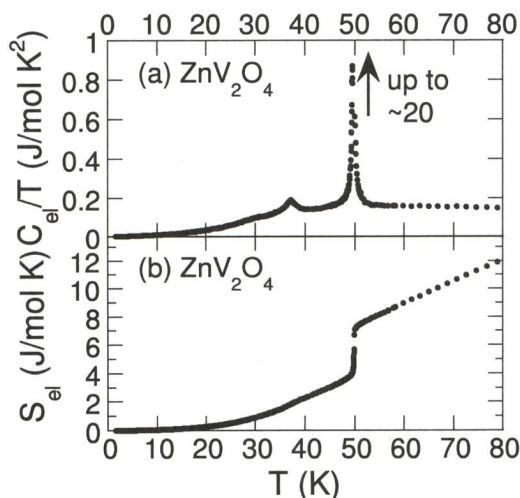

Fig. 3. (a) Electronic specific heat $C_{el}(T)$ divided by T and (b) calculated electronic entropy $S_{el}(T)$ of ZnV_2O_4. The entire peak of $C_{el}(T)/T$ at 50 K is too large to be included in the plot. The values of $S_{el}(T)$ are computed with respect to that at 1.6 K.

$C_{el}(T)/T$ of ZnV_2O_4 shows a diverging peak (to out of the plot) at T_{st}, which in turn exhibits the sudden entropy drop. We can readily identify large entropy remaining for $T_{st} \leq T \ll \theta$. For instance, approximately a half of the total spin entropy $S_{spin} = 2R\log 3$ can be found at $T \approx 60\,K$ (which corresponds to $T/\theta = 0.14$). This gradual release of $S_{el}(T)$ with decreasing T is a characteristic of frustrated spin systems. However, this

vanadate would perhaps have the degenerate orbital degree of freedom. The way the orbital contributes to the observed large entropy is not clear without referencing to the result of the orbitally nondegenerate $ZnCr_2O_4$.

$C_{el}(T)/T$ and $S_{el}(T)$ of $ZnCr_2O_4$ are given in Figs. 4. This result should purely reflect the influence of the spin degree of freedom only. We found the peak in $C_{el}(T)/T$ at 13 K, and the corresponding $S_{el}(T)$ is large and only gradually decreasing above T_N with decreasing T. From Fig. 4(b) we can readily identify, like the vanadate, about a half of the total spin entropy $S_{spin} = 2R\log 4$ at the same T range ($\approx 60\,K$, which is $T/\theta = 0.17$).[29] This behavior is entirely due to geometric frustration.

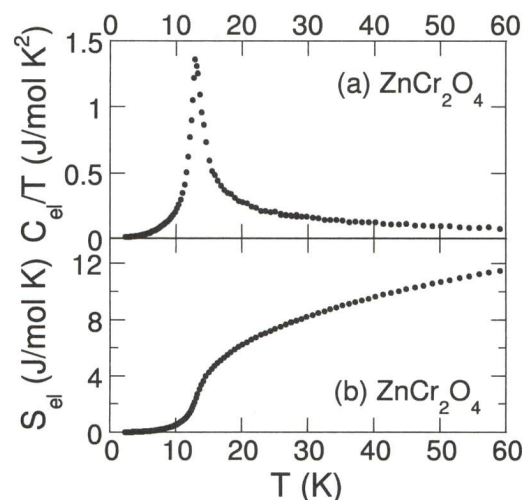Fig. 4. (a) Electronic specific heat $C_{el}(T)$ divided by T and (b) calculated electronic entropy $S_{el}(T)$ of $ZnCr_2O_4$. The values of $S_{el}(T)$ are calculated with respect to that at 2.3 K.

By analogy to the $ZnCr_2O_4$ case, we can conclude that the majority of the large remaining entropy of ZnV_2O_4 is associated with the spin degree of freedom under geometric frustration.

§4. From the frustrated antiferromagnet to the heavy-mass Fermi liquid

We have seen that geometric frustration is found highly influential in the insulating V and Cr spinels. By substituting Zn in the Mott insulator ZnV_2O_4 with Li, it is possible to investigate how differently the strong frustration coordinates the system along with the introduction of doped carriers. In this section, the $C(T)/T$ results on the solid solution series $Li_xZn_{1-x}V_2O_4$ (on polycrystalline samples) are discussed. They are shown in Figs. 5, along with the phase diagram.

For $x = 0.05$, there are still two transitions occurring at two different temperatures like ZnV_2O_4 ($x = 0$). However, as only this little amount of Li is doped, the concurrent suppression of the two transitions is seen, indicative of correlations between spin and lattice.

With more Li doping as $x = 0.3, 0.7–0.9$, the structure no longer undergoes a structural phase transition. This causes the large spin degree of freedom to survive to low T, but along with structural disorder the spin system is
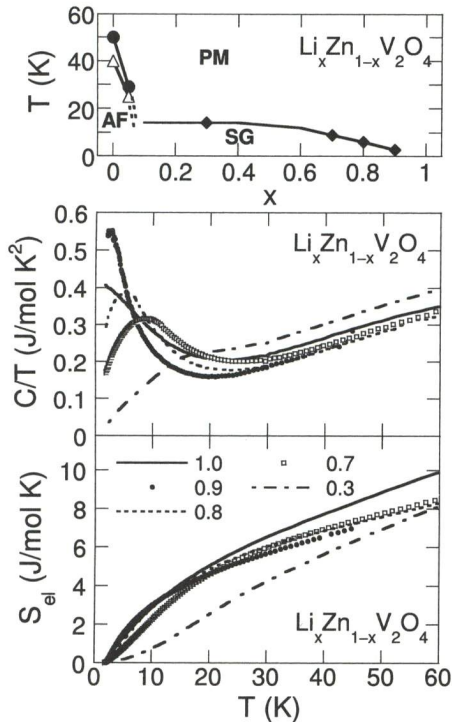
Fig. 5. (a) Magnetic and structural phase diagram of
$Li_xZn_{1-x}V_2O_4$: solid circles, open triangles and solid diamonds
represent structural, antiferromagnetic and spin glass phase
transition temperatures, respectively. For $x = 0, 0.05, 0.3, 0.7–1$,
the symbols are placed according to our susceptibility measure-
ment results.[11] The same diagram was reported by the other
group.[19] (b) Specific heat $C(T)$ divided by T, and (c) calcu-
lated electronic entropy $S_{el}(T)$ are plotted as functions of T.

now frozen below spin glass temperature T_{SG} in this wide
composition range. Hysteretic behaviors were observed
between ZFC and FC magnetizations below T_{SG}. The
T dependence of $C(T)$ in spin glass with geometric frus-
tration differs from that of canonical spin glass where
frustration is caused by random exchange interactions.
$C(T)/T$ of the latter system is independent of T below
$\approx T_{SG}$.[30] Meanwhile, the linear relation $C(T)/T \propto T$
is observed below T_{SG} for the present spin glass system
where geometric frustration prevails. The same T de-
pendence was also seen in other geometrically frustrated
spin glass.[31] T_{SG} decreases progressively as x increases.
At the same time, the peak height of $C(T)/T$ at T_{SG}
becomes larger. The behavior of the electronic entropy
$S_{el}(T)$ appears very similar to each other among all the
spin glass compositions. They all share the large size of
$S_{el}(T)$ above T_{SG}; for example, roughly 70 % of $2R \log 2$
is present at 50 K. With lowering T from above T_{SG},
$S_{el}(T)$ is only slowly released, and when the spin sys-
tem is frozen below T_{SG}, $S_{el}(T)$ starts to decrease more
rapidly.

As approaching the end $x = 1$, T_{SG} goes down. At
$x = 1$ where there is no disorder, the spin glass phase
completely disappears. LiV_2O_4 also retains large $S_{el}(T)$
at high T, comparable to those of the spin glass compo-
sitions near $x = 1$. In addition, the T dependence of the
releasing entropy is quite similar, *i.e.* gradual. However,

unlike the spin glass phase, which releases the residual
entropy more rapidly for $T < T_{SG}$ by quenching spins,
the gradual release of $S_{el}(T)$ for LiV_2O_4 further contin-
ues to $T = 0$. Consequently the persisting geometric
frustration ends with the large γ for LiV_2O_4 at $T = 0$.

§5. Concluding remark

Throughout this paper, we have seen the dominating
influence of the frustrated spin degree of freedom, as-
cribed to the geometric reason of the spinel structure.
It turned out that frustration demonstrates different be-
haviors at low T in the series $(Li, Zn)V_2O_4$: AF order at
the Zn end, spin glass in the intermediate region. For the
Li end, from the continuous change of the observed ther-
mal and magnetic behaviors, it is likely that geometric
frustration plays a certain role to create the heavy quasi-
particle mass.

Concerning the mechanism of heavy mass in LiV_2O_4,
there are attempts to view the system as a dense Kondo
system.[32,33] Among them, Anisimov *et al.* pay a par-
ticular attention to the small but finite trigonal distor-
tion of VO_6 octahedra.[32] Their LDA+U calculations
indicate that the trigonal distortion leads to a splitting
of the t_{2g} bands to the nondegenerate "localized" A_{1g}
and doubly degenerate "itinerant" E_g bands. In this
way LiV_2O_4 mimics dense-Kondo HF systems. In these
studies, geometric frustration is not taken into account
explicitly. It is hard to believe that the close proximity
to the spin glass phase, where the vital role of frustra-
tion is evident, is accidental. Even if the Kondo physics
is essential to the formation of heavy mass, geometric
frustration should be invoked in the unified picture of
ongoing physics.

1) S. Krupička and P. Novák, *Ferromagnetic Materials*, edited
   by E. P. Wohlfarth (North-Holland, New York, 1982), Vol. 3,
   Ch. 4.
2) N. Tsuda, K. Nasu, A. Yanase, and K. Shiratori, *Electronic
   Conduction in Oxides* (Springer-Verlag, Berlin, 1991).
3) D. C. Johnston, J. Low Temp. Phys. **255**, 145 (1976).
4) D. B. Rogers, J. L. Gillson, and T. E. Gier, Solid State Com-
   mun. **5**, 263 (1967).
5) S. Kondo, D. C. Johnston, C. A. Swenson, F. Borsa, A. V. Ma-
   hajan, 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. Chmais-
   sem, and J. D. Jorgensen, Phys. Rev. Lett. **78**, 3729 (1997).
6) N. Fujiwara, H. Yasuoka, and Y. Ueda, Phys. Rev. B **57**, 3539
   (1998).
7) A. V. Mahajan, R. Sala, E. Lee, F. Borsa, S. Kondo, and
   D. C. Johnston, Phys. Rev. B **57**, 8890 (1998).
8) T. Hayakawa, D. Shimada, and N. Tsuda, J. Phys. Soc. Jpn.

58, 2867 (1989), and references therein.

9) R. Ballou, E. Lelièvre-Berna, and B. Fåk, Phys. Rev. Lett. **76**, 2125 (1996).

10) H. Takagi, C. Urano, S. Kondo, M. Nohara, Y. Ueda, T. Shiraki, and T. Okubo, Mater. Sci. Eng. **B63**, 147 (1999).

11) C. Urano, M. Nohara, F. Sakai, M. Koike, H. Takagi, T. Shiraki, and T. Okubo (submitted to Phys. Rev. Lett.).

12) P. W. Anderson, Phys. Rev. **102**, 1008 (1956).

13) S. Kondo, D. C. Johnston, and L. L. Miller, Phys. Rev. B **59**, 2609 (1998).

14) D. C. Johnston, C. A. Swenson, and S. Kondo, Phys. Rev. B **59**, 2627 (1998).

15) In this paper, a 'mol' refers to a mole of formula units.

16) We here denote the Curie-Weiss law as $C/(T + \theta)$.

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

18) S. Niziol, Phys. Status Solidi A **18**, K11 (1973).

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

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

21) S. Kondo *et al.* (unpublished). [The low T powder x-ray diffraction was carried out to MgV_2O_4, isostructural to ZnV_2O_4. These two vanadates are known to display the same physical behaviors.]

22) H. Mamiya, M. Onoda, F. Furubayashi, J. Tang, and I. Nakatani, J. Appl. Phys. **81**, 5289 (1997). [Their work is on the isostructural compound MgV_2O_4.]

23) Y. Kino and B. Lüthi, Solid State Commun. **9**, 805 (1971).

24) T. R. McGuire, L. N. Howard, and J. S. Smart, Ceramic Age **60**, 22 (1952).

25) S. -H. Lee, C. Broholm, T. H. Kim, W. Ratcliff II, and S. -W. Cheong, cond-mat/9908433 v.2 .

26) A. Oleś, Phys. Status Solidi A **3**, 569 (1970).

27) R. Plumier, M. Lecomte, and M. Sougi, J. Phys. (Paris) **38**, L-149 (1977).

28) The lattice specific heat of $LiTi_2O_4$ (Ref. [14]) was used.

29) In the previous specific heat measurement by Plumier *et al.*,[27] the large value of residual entropy can be inferred.

30) L. E. Wenger and P. H. Keesom, Phys. Rev. B **13**, 4053 (1976).

31) A. P. Ramirez, G. P. Espinosa, and A. S. Cooper, Phys. Rev. B **45**, 2505 (1992).

32) V. I. Anisimov, M. A. Korotin, M. Zölfl, T. Pruschke, K. Le Hur, and T. M. Rice, Phys. Rev. Lett. **83**, 364 (1999).

33) H. Kusunose, S. Yotsuhashi, and K. Miyake, cond-mat/9912208.