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LETTER TO THE EDITOR

Staggered magnetism in LiV_2O_4 at low temperatures probed by means of the muon Knight shift

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Abstract
We report on measurement of the muon Knight shift in single crystals of LiV_2O_4. Contrary to what is anticipated for the heavy fermion state based on the Kondo mechanism, the presence of inhomogeneous local magnetic moments is demonstrated by the broad distribution of the Knight shift at temperatures well below the presumed 'Kondo temperature' ($T^* \simeq 30$ K). Moreover, a significant fraction ($\simeq 10\%$) of the specimen gives rise to a second component which is virtually non-magnetic. These observations strongly suggest that the anomalous properties of LiV_2O_4 originate from frustration of local magnetic moments.

(Some figures in this article are in colour only in the electronic version)

As one of the few spinel oxides which exhibit metallic conductivity, LiV_2O_4 provides a unique opportunity to study the potential relation between transport properties and magnetic frustration; the magnetic vanadium ions (nominally $V^{3.5+}$, $3d^{1.5}$) form a three-dimensional network of corner-sharing tetrahedra (pyrochlore sublattice), where antiferromagnetic (AF) correlation between the nearest neighbouring (nn) vanadium moments leads to a highly degenerate magnetic ground state due to geometrical frustration. The emergence of a spin glass-like ground state upon the replacement of Li by Zn strongly suggests that such frustration is indeed occurring [1–3]. In such a situation, it is predicted that an exotic ground state like the resonating valence bond (RVB) state might occur in a system with small spins (e.g., $S = 1/2$) where quantum fluctuation is important [4]. It is well known that the RVB state has been proposed as a possible ground state for the high-T_c cuprate superconductors [5]. Another interesting feature is that there might be a frustration (degeneracy) of the charge state in view

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of the nearly localized electrons; there are a variety of mappings for the V^{3+} and V^{4+} ions which are energetically equivalent on the pyrochlore lattice.

Meanwhile, the recent revelation of a heavy fermion-like behaviour in LiV_2O_4 has stimulated renewed interest in this compound, where the large Sommerfeld coefficient at low temperatures ($\gamma \simeq 0.42$ J^{-1} mol^{-1} K^{-2}), comparable to that of typical f electron heavy fermion compounds, e.g, UPt_3, has been attributed to the formation of d electron heavy quasiparticles [3, 6, 7]. Besides the Sommerfeld coefficient, other bulk properties including spin susceptibility, resistivity and the Hall coefficient commonly suggest a characteristic temperature, $T^* \simeq 30$ K, where the formation of such a coherent fermionic state seems to set in.

It is established in the f electron heavy fermion systems, particularly in those belonging to the class of 'dense Kondo' systems, that the heavy quasiparticles are formed by the Kondo coupling between conduction electrons and local f electrons, where the local spin degree of freedom is convoluted into the effective mass of conduction electrons through spin singlet formation. Therefore, provided that a similar electronic state is realized in LiV_2O_4, there would be no possibility for the geometrical frustration to play a role in the electronic properties; the ground state would be a uniform metallic state without local magnetic moments. However, it is not obvious whether or not such a heavy quasiparticle state is possible in transition metal oxides, because the metallic conduction is carried by d electrons which exhibit strong local electronic correlation.

In this brief communication, we report on our recent measurement of the muon Knight shift in single-crystalline (sc-) LiV_2O_4. In the previous study on the powder specimen, we have shown that there are two different magnetic sectors which are greatly different in their dynamical properties [8]. In particular, one of these exhibits a relatively large hyperfine coupling with a broad distribution at lower temperatures which is fluctuating with a characteristic frequency of 10^9–10^{12} s^{-1}. Here we show that the fractional yield of this magnetically fluctuating component is further enhanced in the single-crystalline specimen, while the non-magnetic sector remains as a minority component. This observation clearly demonstrates that the presence of local moments is an intrinsic property of LiV_2O_4, and thereby it strongly suggests that the excess entropy is carried mostly by the frustrated local spins at lower temperatures.

It is often found in the Li compounds that the specimen exhibits rapid deterioration due to the migration of Li atoms and subsequent oxidization at the surface. This can be avoided by the use of a large single crystal to minimize the surface area. However, the crystal growth of LiV_2O_4 is quite limited due to chemical difficulties; so far it is only the hydrothermal method that has been successful in the growth of sc-LiV_2O_4 [9]. Unfortunately, the hydrothermal method is not suited for large and high yield crystal growth in the laboratory because of the difficulty of optimizing conditions. Moreover, it has a greater possibility of Li deficiency in the crystal. We have succeeded in growing single crystals with a dimension of $\sim$1 mm^3 using the $LiCl$–Li_2MoO_4–$LiBO_2$ system as a solvent for LiV_2O_4 [10]. The crystals obtained exhibit bulk properties which are in perfect agreement with those reported earlier [3]. In order to avoid deterioration due to exposure to ambient conditions in transit, the crystalline specimen (consisting of small crystals with a net weight of $\sim$0.1 g) was encapsulated in an evacuated vial immediately after the growth.

μSR measurements under a transverse field ($\simeq$10 kOe) have been performed on the M15 beamline of TRIUMF using the HiTime spectrometer. The crystal specimen was loaded onto a He gas-exchange-type cryostat, and irradiated with a muon beam with a momentum of 29 MeV/c; the muon stopping range is $\sim$0.5 mm at this momentum and thereby muons probe the bulk crystal properties. Precautions were taken to minimize the duration of exposure to the
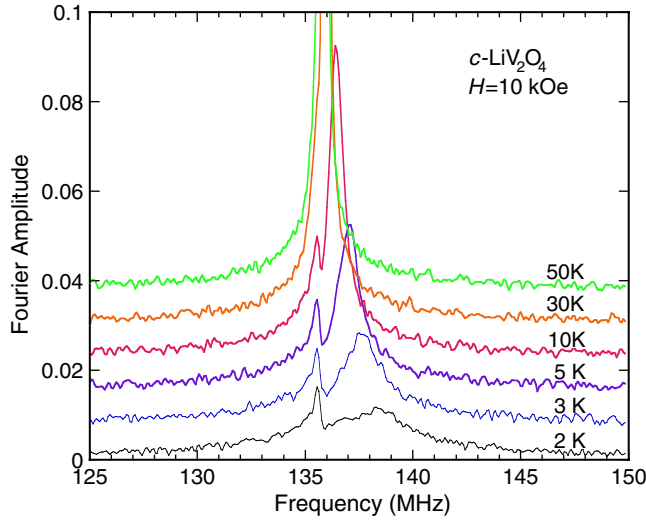
Figure 1. The fast Fourier transform of the μSR time spectra in crystalline LiV_2O_4 at low temperatures. The peak near 135 MHz remains sharp, while another peak at higher frequency becomes broad with decreasing temperature.

air while loading the specimen from the vial. A low background decay-positron counter system was employed to reduce the positron events arising from muons which missed the specimen. The relative background yield is expected to be less than ~5% in typical conditions.

The fast Fourier transform of the μSR time spectra at low temperatures is shown in figure 1, where a double-peak structure is clearly observable below 10 K; detailed examination indicates that the structure due to the satellite peak at lower frequency is already visible at 50 K. While the position and linewidth of the satellite peak (near 135 MHz) are mostly independent of temperature, the main peak exhibits a shift to higher frequency and an associated increase of the linewidth with decreasing temperature, indicating that the latter has a much stronger hyperfine (HF) coupling with considerable distribution of the coupling parameters. These features are qualitatively in perfect agreement with those observed previously for the powder specimen [8]. It is notable, however, that a considerable shift of the signal weight from the former to the latter component is observed for sc-LiV_2O_4. Moreover, the linewidth of the latter component is considerably larger than that of the powder specimen. The fitting analysis in the time domain using the form

$$A_0 G_{xy}(t) = A_0 e^{-i\phi} \sum_{i=1}^{n} f_i \exp(i\omega_i t - \Lambda_i t), \tag{1}$$

indicates that the spectrum is well reproduced by assuming three frequency components ($n = 3$), where the main peak is further split into a doublet; here A_0 is the muon–positron decay asymmetry, f_i is the fractional yield of the component ($\sum f_i = 1$) with a frequency ω_i and relaxation rate Λ_i, and ϕ is the initial phase.

Figure 2(a) shows the temperature dependence of the peak frequency ω_i with the temperature plotted on a logarithmic scale. Compared with that of the bulk susceptibility (χ) shown in figure 2(b), ω_2 and ω_3 (corresponding to the broad peak in figure 1) exhibit steep increases over the temperature region below $T^* \sim 30$ K where the susceptibility levels off. Here, we stress that the temperature dependence of the bulk χ is in excellent agreement with that reported previously for a single-crystal specimen [3]. The behaviour of $\omega_{2,3}$ indicates that the local susceptibility probed by means of the muon Knight shift is not proportional to the bulk susceptibility below T^*. In accordance with the muon Knight shift, the spin relaxation rate of the broad peak increases steeply with decreasing temperature (see figure 3(a)). It is known
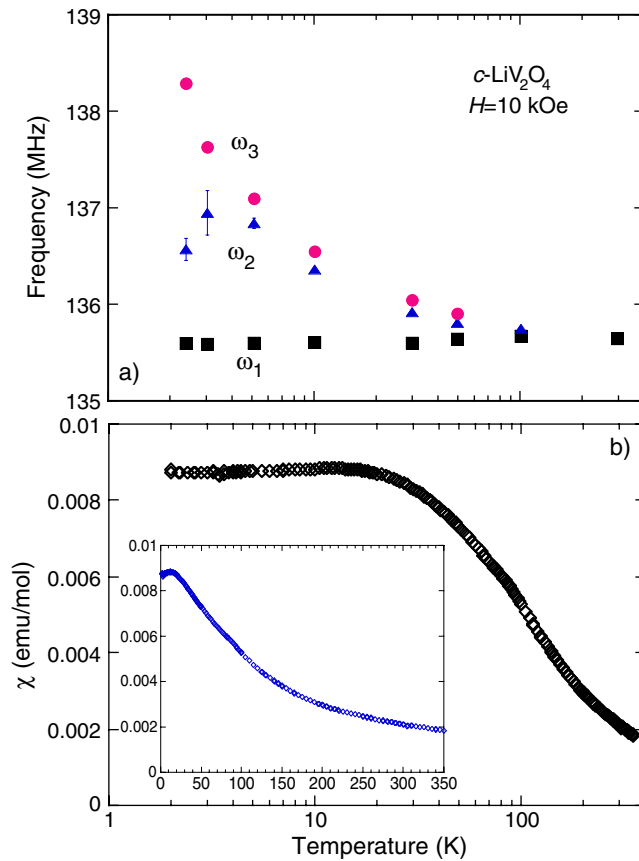
Figure 2. (a) The frequency of three components versus temperature obtained by fitting analysis using equation (1), where the abscissa has a logarithmic scale. (b) The temperature dependence of the magnetization in the present specimen. Inset: the same data displayed on a linear scale.

from the previous μSR experiment under a longitudinal magnetic field that the longitudinal spin relaxation is slow over the relevant temperature region due to the fast fluctuation of HF fields [8]. Therefore, the broad linewidth under a transverse field can be attributed to the distribution of HF parameters, which is naturally expected for the case of staggered magnetism.

In contrast to the behaviour of the frequency shift which is markedly different above and below T^*, the temperature dependence of the partial asymmetry for the broad peak (i.e., $A_0[f_2 + f_3]$ in figure 3(b)) resembles that of χ; it develops gradually below ambient temperature and levels off around T^*. The fractional yield of the broad peak ($f_2 + f_3$) at low temperatures is about 90%, which is considerably larger than that observed for the powder specimen (~50%) [8]. Considering the quality of the present specimen, this result strongly suggests that the bulk electronic property is predominantly determined by the staggered magnetism. On the other hand, while the yield of the satellite peak (f_1) exhibits a gradual decrease with decreasing temperature, it stays near ~10% at low temperatures. This is considerably larger than the background level of the experimental apparatus, and thereby we attribute this component to the signal from the specimen. It is interesting to note that such partitioning of the μSR signal into two components is commonly observed for Zn-doped LiV_2O_4 [8, 11]. The significant difference in relative yield of those components between powder and single-crystalline specimens strongly suggests that the magnetic properties of LiV_2O_4 are sensitive to the quality of the specimen and that all the previous results based on powder specimens should be re-examined in this respect [12, 13].
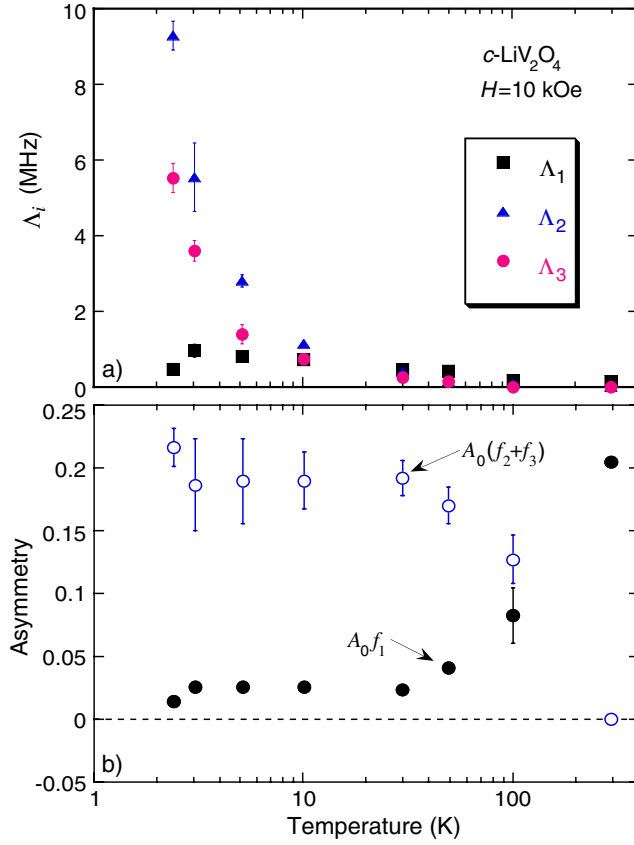
Figure 3. (a) The spin relaxation rate and (b) the partial asymmetry of three components versus temperature obtained by fitting analysis using equation (1), where the sum $A_0(f_2 + f_3)$ in (b) corresponds to the net asymmetry for the broad peak.

In order to examine the HF parameters in more detail, the muon Knight shift (K_μ^z) is plotted against the bulk magnetic susceptibility in figure 4. Note that the gradient in this $K-\chi$ plot provides the muon HF parameter,

$$A_\mu^z = N_A \mu_B \frac{dK_\mu^z}{d\chi}, \tag{2}$$

where N_A is the Avogadro number and μ_B is the Bohr magneton. As was anticipated from figure 2, the $K-\chi$ relation is highly non-linear for the broad components (corresponding to ω_2 and ω_3), while that for the satellite line (ω_1) exhibits a linear relation with a small negative gradient corresponding to $A_\mu^z \simeq -0.40$ kOe/μ_B. This is in good contrast to the typical behaviour observed for conventional heavy fermion compounds, e.g., CeRu$_2$Si$_2$ ($T^* \sim 10$ K) [14], where no such anomaly is observed. In terms of the broad component, the previous result obtained for the powder specimen [8] (dashed lines in figure 4) seems to be a coarse average of the behaviours observed for sc-LiV$_2$O$_4$. Thus, a broad distribution of the HF parameter below T^* is confirmed from this non-linear behaviour of the $K-\chi$ plot. In the meantime, the calculated value of A_μ^z shows reasonable agreement with the mean value of A_μ^z (~ 6 kOe/μ_B) at the lowest temperature when the muon site is assumed to be slightly off the centre of a ring consisting of six V^{4+} ions (with their full moment in effect) to form a muon–oxygen bond ($\simeq 1$ Å); the reason for not considering the contribution of V^{3+} is discussed below.

It is inferred from the large HF parameter as well as its broad distribution ($\Delta A_\mu^z \sim 3$ kOe/μ_B) observed for the predominant component that there are staggered magnetic moments
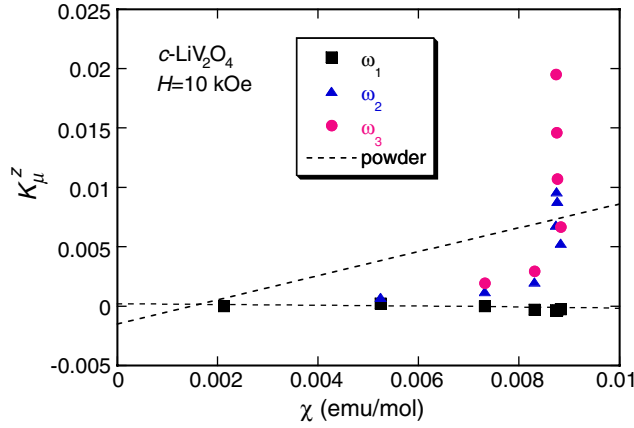
Figure 4. The muon Knight shift versus magnetic susceptibility ($K-\chi$ plot) obtained from the data in figure 2. The dashed lines indicate the previous result on the powder specimen, where $A_\mu^z = +5.57\,\text{kOe}/\mu_B$ and $-0.27\text{kOe}/\mu_B$ (after [8]).

of vanadium ions in LiV_2O_4 at temperatures well below the presumed Kondo temperature ($\sim T^*$). This is quite different from what is expected for the conventional Kondo lattice system where the local moments are quenched by the Kondo coupling to the conduction electrons. Thus, the present μSR result is clearly inconsistent with the theoretical models which assume the disappearance of local moments due to the Kondo effect or other mechanisms [15–19]. On the contrary, it strongly suggests that the heavy fermion-like behaviour observed for the bulk electronic property is superficial, and that it is due to the macroscopic degeneracy of the states associated with the geometrical frustration of local vanadium moments [20]. Along these lines, a number of theoretical attempts have been made to understand the true ground state of LiV_2O_4 [21–25]. The conjecture is based on the nearly localized V^{3+} and V^{4+} ions which undergo valence fluctuation; it is interesting to note that the situation, in terms of the charge state, is similar to that considered by Verwey for magnetite (Fe_3O_4) [26]. Then, considering Anderson's argument that the two-by-two occupation of V^{3+} and V^{4+} ions on a tetrahedron is most favourable in terms of free energy [27], the entire pyrochlore lattice can be viewed as a cluster of one-dimensional chains/rings consisting only of V^{3+} or V^{4+} [22]. An example of such a situation is illustrated in figure 5. Here, the trivalent vanadium ions ($S = 1$) correspond to the Haldane chains, and thus they would be in spin singlet states. Meanwhile, the tetravalent vanadium ions ($S = 1/2$) would give rise to the Heisenberg spin chains of local moments which would remain paramagnetic at low temperatures. Presumably the latter effect is responsible for the highly enhanced Sommerfeld coefficient of LiV_2O_4 due to the entropy associated with the staggered moments [20], while the states exhibiting the former effect are predicted to have a Haldane gap and thereby would not contribute to the low energy excitation.

We point out that the observed μSR signals are perfectly in line with the above-mentioned ground state; the sharp satellite peak (which is virtually non-magnetic) might be the signal coming from the muons surrounded by the Haldane chains, and the broad peaks might be from those near the Heisenberg spin chains. The small hyperfine parameter for the former is attributed to the dipolar coupling between muons and paramagnetic spins at the edge of the Haldane chains [28, 29], which would exhibit normal $K-\chi$ behaviour. On the other hand, the linewidth for the latter would be controlled by the valence (charge) fluctuation rate ν_C; when ν_C falls below $10^9\,\text{s}^{-1}$, the difference in configuration of V^{3+}/V^{4+} ions around the muon sites would lead to the distribution of hyperfine parameters ΔA_μ^z because the time-averaging mechanism becomes ineffective. Here, we speculate that $\nu_C \leqslant 10^9\,\text{s}^{-1}$ below ~ 10 K (close to the charge order), irrespective of the spin fluctuation rate ν_D ($\geqslant 10^9\,\text{s}^{-1}$) which is independent
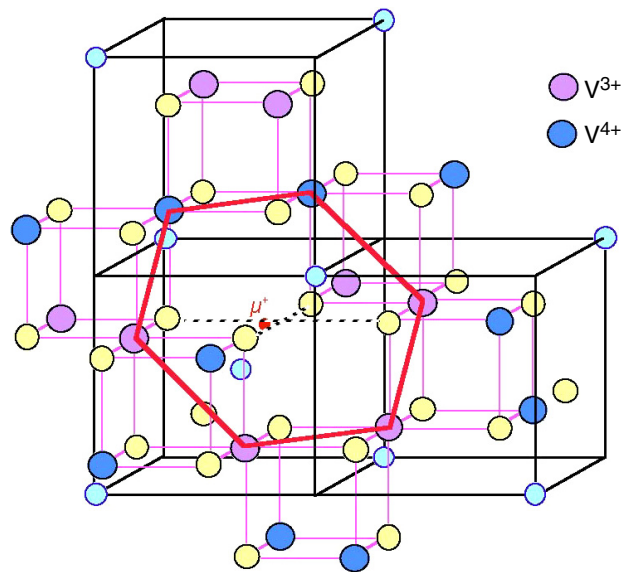
Figure 5. One of the possible configurations of V^{3+} and V^{4+} ions which satisfy the rule that every vanadium tetrahedron has two of them each. Muons are likely to be situated near the centre of an octahedral cage made of oxygen atoms. The six nearest neighbouring vanadium ions are marked by a solid hexagon, where four of them belong to a Haldane chain (consisting of V^{3+} ions) and the rest to a Heisenberg chain.

of temperature as inferred from the previous μSR study under a longitudinal field [8]. The non-linear behaviour in the $K-\chi$ plot might be thus understood as a dynamical change of A_μ^z induced by the slowing down of the valence fluctuation. It is also true, however, that LiV_2O_4 is a metallic system and thereby the above interpretation would be an oversimplified view of the actual situation.

The non-linear behaviour of $K-\chi$ relation is occasionally found in various magnetic systems including pyrochlore oxides [30], where the anomaly is attributed to impurities or muon-induced local perturbation of electronic states (i.e., muons serving as impurities). However, we presume that such an effect would be negligibly small in metallic LiV_2O_4 for the following reasons. First, the positive charge brought in by the muon is screened by conduction electrons in metallic systems so the local modification of the electronic state would be negligible. Secondly, it happens that there is a large space available in the spinel structure to accommodate muons; as mentioned earlier, muons are probably sitting near the centre of large octahedral cages cornered by oxygen atoms (see figure 5). Then the change in the elastic energy due to accommodation of muons would be small, although there is no quantitative estimate at this stage.

Finally, we briefly examine how consistent our μSR result is with those obtained using other microscopic probes. An apparent discrepancy arises from the fact that $^{51}V/^7Li$ nuclear magnetic resonance (NMR) studies report only a single frequency component [2, 12, 31–34], whereas at least two components were observed in μSR. As discussed in the previous report [8], however, this can be readily understood from the difference in the frequency window of the sensitivity. It happens that the relaxation rate of the satellite peak (Λ_1) is of the order of ~ 1 MHz, which might mask the NMR signal. The appearance of ΔA_μ^z and associated non-linear behaviour of $K-\chi$ in the main peak might be irrelevant for NMR as long as $\nu_C \gg 10^6 \, s^{-1}$,

so the hyperfine coupling may be averaged over the timescale of the NMR. Concerning the results from neutron scattering, the most recent report suggests the presence of two components with different dynamical characters [35]. Thus, it seems that the ground state of LiV_2O_4 revealed by μSR is consistent with the current experimental knowledge of this compound.

In summary, we have demonstrated that the ground state of LiV_2O_4 is characterized by staggered magnetism at low temperatures, where the presence of local magnetic moments has been established. While such a ground state may be explained by the valence fluctuating vanadium ions close to localization, it is inconsistent with the prediction of a conventional heavy fermion state based on the Kondo scenario. In order to reconcile the metallic behaviour as a bulk property with that revealed by the present μSR study, further progress in the theoretical understanding is clearly needed.

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