Metallic Spin Liquid-like Behavior of LiV$_2$O$_4$

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LiV$_2$O$_4$ spinel is known to exhibit heavy fermion-like behavior below a characteristic temperature $T_K \approx 20$ K, while it preserves a paramagnetic state down to $T \sim 10^{-2}$ K due to geometrical frustration. Here, it is shown that the dynamical spin susceptibility $\chi(q,\omega)$ in LiV$_2$O$_4$ exhibits anomalous duality which is modeled as a sum of itinerant ($\chi_I$) and local ($\chi_L$) components, and that the local spin dynamics inferred from $\chi_L(q,\omega)$ is qualitatively different from that expected from time-averaged bulk properties. The anomaly coexists with the marginal Fermi liquid behavior inferred from the $-\ln T$ dependence of the electronic specific heat over a wide temperature range below $T_K$. We argue that such unusual properties of LiV$_2$O$_4$ can be attributed to the putative metallic spin glass state emerging near the quantum critical point between spin glass and Fermi liquid states.

Quantum phase transition and associated critical behavior of electronic states has been a central focus of condensed matter physics in the past decades [1]. The quantum fluctuation induces various anomalies to the electronic properties at finite temperatures, serving as a promising ground in hunting for novel states of matter. In particular, the “metallic spin liquid” state (or spin liquid metal) is attracting much interest as a novel non-Fermi liquid state in the field of $f$-electron systems, where it is predicted to emerge near the quantum critical point (QCP) next to the metallic spin glass state [2-4].

The metallic spin liquid comprises a counterpart of the “spin liquid” in insulators. While the spin liquid is characterized by disappearance of paramagnetism (as local electron spins fall into a collective singlet ground state), the metallic spin liquid exhibits paramagnetism linked to spin glass. The ultimate conflict between the strong electronic correlation (preferring magnetic order) and the Kondo effect (driving to the Fermi liquid) may lead to quantum criticality and associated novel metallic state, where the coupling between spin and charge fluctuation is largely different from the insulating spin liquid [5-6]. It is also noticeable that the metallic spin glass/liquid is intensively discussed as a stage of the metallic spin liquid [1]. In this regard, it is noteworthy that certain $f$-electron compounds known to date, i.e., Y(Sc)Mn$_2$ [7, 9] and LiV$_2$O$_4$ [2-4] have a common feature that the transition metal ions comprise the pyrochlore lattice and therefore subject to the geometrical frustration, as inferred from the emergence of metallic spin glass upon chemical pressure [15, 16]. In fact, alienation from the Fermi liquid was indeed suggested by “$-\ln T$” dependence of $\gamma$ (i.e., the marginal Fermi liquid behavior regarding the conduction electrons) and anomalous magnetic field dependence of $^7$Li-NMR for powder samples of LiV$_2$O$_4$ [19, 20].

This motivates us to reexamine the currently prevailing consensus of LiV$_2$O$_4$ as a typical heavy fermion (HF) metal from the viewpoint of metallic spin glass/liquid. While certain bulk properties ($\rho$, $\chi_{\text{bulk}}$) and the Köringa law indicated by $^7$Li-NMR suggest Fermi liquid state [15, 21, 22], muon spin rotation ($\mu$SR) [18, 24], $^{51}$V-NMR [21, 25], and inelastic neutron scattering (INS) [26-28] coherently imply presence of localized $d$ electrons even below a characteristic temperature $T_K \approx 20$ K where the $-\ln T$ behavior for $\gamma$ develops. New theoretical framework beyond the canonical Kondo lattice model is called for, since inter-site interactions including the Coulomb and AF correlations clearly pertains to the anomaly [4, 29].

We report $\mu$SR study on high-quality LiV$_2$O$_4$ samples that provides crucial information on the dynamical spin susceptibility $[\chi(q,\omega) = \chi'(q,\omega) + i\chi''(q,\omega)]$. The muon Knight shift ($K_\mu$) and longitudinal depolarization rate ($1/T_\parallel^\text{L}$) were measured simultaneously on the same sample to entirely eliminate the sample dependence and aging problem. Appropriate choice of external magnetic field ($B_0 \leq 0.5$ T) allowed determination of $K_\mu$ with improved precision by controlling the transverse linewidth ($1/T_\parallel^\text{T}$). We show that both $K_\mu$ and $1/T_\parallel^\text{L}$ are dominated by paramagnetism, and that $1/T_\parallel^\text{T}$ is anomalously enhanced by $B_0$. These features are commonly observed in the paramagnetic state of canonical dilute spin glass systems like AgMn [30], which is in marked contrast with the HF-like properties. We further demonstrate that such dichotomy is understood by a phenomenological model in
which $\chi(q, \omega)$ is described by a sum of itinerant ($\chi_I$) and local ($\chi_L$) spin components, to which the relevant probes exhibit complementary sensitivity. The behavior of $\chi_L$, inferred from $K_\mu$ and $1/T_1^\mu$ is qualitatively in line with that of the local susceptibility predicted for the metallic spin liquid [19].

The Fourier transform of the time-dependent $\mu$SR spectra $A_i(t)$ for a transverse field $B_0 = 0.1$ T, and the parameters deduced from curve-fits for the spectra under $B_0 = 0.1$ and $0.5$ T are shown in Fig. 1 where the previous data on another set of high quality single-crystalline (sc-) LiV$_2$O$_4$ samples under $B_0 = 1$ T [24] are also plotted. (For the details on samples and $\mu$SR experiment, see Supplemental Material [31]) The muon Knight shift exhibits a divergent behavior that is in marked contrast with $\chi_{\text{bulk}}$, and splits into two components, $K_{\mu 0}$ and $K_{\mu 1}$, below $~10^5$ K with relative signal amplitude of $~10\%$ or less for $K_{\mu 0}$ (see Fig. 1b). In addition, $1/T_2^\mu$ concomitantly exhibits strong enhancement with increasing $B_0$, where the lineshape at 1 T (not shown) is better represented by assuming further splitting (with $K_{\mu 2} < K_{\mu 1}$). In contrast, the spectra under a longitudinal field (LF) showed least dependence on the magnitude of $B_0$, as is evident in Fig. 1h (except for the change between 0 and 10 mT corresponding to the quenching of quasi-static nuclear dipolar fields under a weak LF). Because of the relatively small amplitude for $K_{\mu 0}$ that tends to decrease with improved sample quality, we attribute this component to an unknown extrinsic phase and focus on the $K_{\mu} \equiv K_{\mu 1}$ component below (with $1/T_2^\mu \equiv 1/T_2^{\mu \parallel}$).

The spin part of the Knight shift is given by $K_{\mu} = A_{\mu 0} \chi'(0,0)/(N_A\mu_B)$, where the label $\alpha$ is introduced for distinguishing the cases of $\mu$SR ($\alpha = \mu$) and $\mu$NMR ($\alpha = I$). $A_{\mu 0}$ is the $q = 0$ component of the $q$-dependent hyperfine parameter $A_{\mu q}$, $N_A$ is the Avogadro number, and $\mu_B$ is the Bohr magneton. A curve-fit analysis of the shift at 0.1 T by the Curie-Weiss law, $K_{\mu} \propto 1/(T + \theta_\mu)$, yields excellent fit (dashed curve in Fig. 1b) with a Weiss temperature as small as $\theta_\mu = 1.79(1)$ K. Another excellent fit is obtained by $K_{\mu} \propto -\ln T$ for the data below 10 K (solid curve in Fig. 1b). For comparison, also plotted in Fig. 1b are the shifts corresponding to $\chi_{\text{bulk}}$, $K_{\mu 0} = A_{\mu 0}\chi_{\text{bulk}}/N_A\mu_B$, and to $\chi_\mu = \chi(q,0)$ obtained from INS [26]. $K_{\chi q} = A_{\mu 0}\chi_q/N_A\mu_B$ with $Q_q = (0.6$ Å$^{-1}$ being the $q$ vector characterizing the spatial correlation of the predominant magnetic fluctuation), where $A_{\mu 0} = 0.1658$ T/µB was evaluated using the dipolar tensor for the known 16c site [13, 21]. While $K_{\mu 0}$ and $K_{\mu}$ [21] are in nearly perfect agreement with each other, $K_{\mu}$ exhibits remarkable deviation from these for $T \ll T_K$ with a certain similarity to $K_{\chi q}$. It must be noted that $K_{\mu 0}$ exhibits the Curie-Weiss behavior only for $T > T_K$ with a Weiss temperature $\theta_W = 60$ K, which is much greater than $\theta_\mu$.

It is indicated from Fig. 1b that $1/T_2^\mu$ is strongly enhanced by $B_0$, whereas $1/T_1^I$ ($\propto \chi''$) is mostly independent of field (see Fig. 1a) [19], suggesting that the linewidth is dominated by the static distribution of shift, $\Delta K_{\mu} \propto \Delta \chi'$, i.e., $(1/T_2^\mu)^2 \approx (1/T_1^I)^2 + (\Delta K_{\mu} B_0)^2$. These features are in remarkable similarity with that observed in the paramagnetic state ($T > T_g$, the glass temperature) of diluted metallic spin glass systems (e.g., AgMn) [22], suggesting the common origin for the anomalous field-induced inhomogeneity of $\chi'$. Similar anomalies are reported from an earlier $^7$Li-NMR study under a relatively low $B_0$ [19].

The hyperfine interaction at the muon site ($\bar{3}d$, trigonal) generally consists of two components, i.e., magnetic dipolar interaction ($A_{0 \mu}^\mu$) with local electrons and transferred hyperfine interaction ($A_{I \mu}^\mu$) with itinerant electrons, where the latter is presumed to yield a minor contribution for muon at interstitial sites. Considering the possibility for these interactions to couple with different components of the local susceptibility, we introduce a phenomenological model in which $\chi$ consists of two parts, i.e., $\chi_{\sigma}(q, \omega)$ with $\sigma = F$ and $L$ [31]. We employ the conventional Lorentzian form with two components,

$$\chi_{\sigma}(q, \omega) = \frac{\chi_{\sigma 0}}{1 + \left(\frac{\omega - q \sigma \nu_{\text{r}}}{\Gamma_{\sigma}}\right)^2} = \chi_{\sigma}^{\prime}(q, \omega) + i\chi_{\sigma}^{\prime\prime}(q, \omega), \quad (1)$$

where $\chi_{\sigma 0} = \chi_{\sigma}(q, 0)$ is the static susceptibility, $\Gamma_{\sigma}$ is the magnetic relaxation rate, and $\nu_{\text{r}}$ is the linewidth. The metallic spin liquid-like behavior described by a local form [$\chi_{\text{loc}}(\omega)$] [3, 3] is presumed to be monitored by the $q$-independent parameters. The Knight shift is then described as

$$K_{\mu} \approx \frac{1}{N_A\mu_B} \sum_{\sigma = F, L} A_{0 \mu}^{\sigma \mu} \chi_{\sigma 0}, \quad (2)$$

where $\chi_{\sigma 0}^{\prime} = \chi_{\sigma}^{\prime}(0, 0) = \chi_{\sigma 0}/[1 + |Q_q|^2/(\nu_{\text{r}})^2]$. Note that the transferred hyperfine interaction dominates for $^7$Li-NMR due
to the cubic symmetry of the Li site, so that $K_I = A_{A_0}^0 \gamma_F^c / N_A \mu_B$ [23]. Thus, it is interpreted that $K_I$ in Fig. 1b represents the contribution of $\chi_{F_5}$, and that $K_\mu$ is predominantly determined by $\chi_{L_5}$ for $T < T_K$ where $K_\mu \approx A_{A_0}^0 \gamma_F^c / N_A \mu_B$. The temperature dependence of $K_\mu$ suggests that $\chi_L(q, \omega)$ represents a strongly localized component of the electronic state, which is in line with the dominant role of magnetic dipolar interaction for $A_{A_0}^0 (\approx A_{A0})$.

A similar situation is observed for the magnetic relaxation rate among different probes. As shown in Fig. 2b, $1/T_1^g$ exhibits a tendency of gradual increase and subsequent leveling-off with decreasing temperature, which is in marked contrast with the case of NMR where $1/T_1^s$ obeys the Korringa relation ($\propto T$) over the relevant temperature region [22,23]. The longitudinal depolarization rate is obtained using $\chi_{F_5}^c(q, \omega)$,

$$\frac{1}{T_1^g} = \frac{k_B T}{N_A \mu_B} \sum_{q_{ex} \in F_5} \left( \frac{\gamma_A A_{A_0}^0}{\omega_0} + 1 + \left( q - Q_s \right)^2 / (\kappa^c)^2 \right) |\Gamma^c(q)|^2,$$

(3)

where $\omega_0 = \gamma_A B_0$. To compare the temperature dependence of $q$-averaged $\Gamma^c(q) (= \nu^c)$ with that deduced from INS ($\Gamma_4^\nu$), which is predominantly determined by $q = Q_s$, we define the $q$-averaged quantities, $2(\delta q)^2$ for $\gamma_A A_{A_0}^0$ and, take an approximation of Eq. (3) to deduce $\nu^c$ from $1/T_1^g$,

$$\frac{1}{T_1^g} \approx \frac{k_B T}{N_A \mu_B} \frac{2(\delta q)^2}{\nu^c},$$

(4)

$$\frac{1}{T_1^s} \approx \frac{k_B T}{N_A \mu_B} \frac{2(\delta q)^2}{\nu^c},$$

(5)

where the contribution of $\chi_{L_5}$ to $1/T_1^g$ as well as that of $\chi_{F_5}$ to $1/T_1^s$ becomes negligible because $\delta q^c (\propto A_{A_0}^0)$ and $\delta q^s (\propto A_{A0}^c)$ are small (as inferred from $K_\mu$). (As shown below, the result of the numerical analysis is consistent with the presumption that $\omega_1, \omega_2 \ll \nu^c, \nu^s$.) In addition, the large difference in the sensitive range of $1/T_1^g$ between NMR ($1/T_1^g \leq 10^6$ s$^{-1}$) and $\mu$SR ($1/T_1^g \geq 10^4$ s$^{-1}$) must be considered [22].

For the NMR part, using the reported hyperfine field for $^7$Li nuclei ($\delta q^c = 17.8-26.9$ MHz/$\mu_B$, $\chi_{bulk}$ for $\chi_{F_5}$, and the Korringa relation, $1/T_1^g \propto T \simeq 2.0-2.5$ s$^{-1}$K$^{-1}$ over a low temperature region $0.5 \leq T \leq 4.2$ K [23]), $\nu^c$ is estimated from Eq. (3) to be $\simeq 10^{13}$ s$^{-1}$ (shown as a hatched area in Fig. 2b). This is in reasonable agreement with that expected for the presumed HF quasiparticle state, $\nu_F \approx 2\nu c_{F_5}^c / N_A / 3h \gamma = 1.7 \times 10^{13}$ s$^{-1}$ for $\gamma = 0.42$ J/mol/K$^2$ observed at 2 K, in support for the model that $\chi_F(q, \omega)$ corresponds to the itinerant part of the electronic state.

For the self-contained evaluation of $\nu^c$, we note the relation $\chi_{L_5} / \chi_{F_5} = 1 + |Q_s|^2 / (\kappa^c)^2$ between $\chi_{L_5}$ and $\chi_{F_5}$ in Eqs. (2) and (3). We can further expect that $\Gamma^c(q) / \Gamma^g(Q_s) \approx 1 + (q - Q_s)^2 / (\kappa^c)^2$ for the local spin systems. Considering that these deviations from unity in proportionality tend to cancel through the $q$-average in Eq. (3), we may reasonably assume that substitution of $\chi_{L_5}$ in Eq. (5) with $\chi_{F_5}$ as a better $q$-average. The magnetic relaxation rate $\nu^c$ is then deduced from $K_\mu$ and $1/T_1^g$ at 0.1 T $\delta q^c \approx \gamma_A A_{A_0} = 141.2$ MHz/$\mu_B$. As shown in Fig. 2b, the qualitative agreement between $\nu^L$ and $\Gamma_4^\nu$ for $T \geq 1.6$ K, in addition to the similarity between $K_\mu$ and $K_{\chi_L}$, provides evidence that both $\mu$SR and INS mainly probe $\chi_L$. More importantly, $\nu^c$ exhibits a general trend of decrease with decreasing temperature (except for a slight re-mention around 5 K, which we discuss later). For allowing a wider scope for the temperature range, we quote our previous result obtained for a powder specimen cooled down to $\sim 0.02$ K, in which one of the two signals showing greater depolarization rate ($\lambda_D$ in Ref. [18]) turns out to be the relevant component [22]. As is evident in Fig. 2b, these two sets of data show smooth overlap with each other, supporting our presumption that $\lambda_D$ represents an intrinsic property. (This owes to the merit of $\mu$SR as a local probe, with which we can readily distinguish the origin of signals between LiV$_2$O$_4$ and other secondary phases.) It is now clear that $\nu^c$ [dominated by $\Gamma^c(Q_s)$] exhibits a power law ($\nu^c \propto T^{\alpha}$ with $\alpha \approx 1$) below $\sim 5$ K over $2-3$ decades in temperature. Such behavior indicates that the Kondo screening is incomplete for the $\chi_L$ component, as it has been suggested by absence of $-\ln T$ dependence in $\mu$SR ($\nu^L$) [13].

Previously, the deviation of $\chi_L$ from the Curie-Weiss law observed by INS for $T < T_K$ (shown by $K_{\chi_L}$ in Fig. 1b) was interpreted as a sign for the development of the Kondo screening [22]. However, the recent INS experiment on sc-LiV$_2$O$_4$ showed emergence of the second component around $Q_s$ with a relatively broader $\kappa$ [23] that might have been overlooked as background in the previous experiment, leading to the under-
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The behavior of \( \chi_L \) suggests strong interaction of local spins with the marginal Fermi liquid portion corresponding to \( \chi_F \) via hybridization and possibly double-exchange interaction (a higher order effect of the Hund coupling). The competition between the Hund coupling and AF correlation via direct exchange interaction may be the origin of the secondary energy scale \( \gamma_0 \). While this reminds us of the second component of \( \chi(q, \omega) \) observed by INS, it cannot be simply attributed to \( \chi_F \) considering the orders of magnitude difference in the spin fluctuation rate (\( \gamma^L \) vs \( \gamma^F \)).

Finally, we point out that the monotonic decrease of \( \nu^L \) with decreasing temperatures should entail anomalous response of \( \chi_L(q, \omega) \) to the external magnetic field at lower temperatures where \( \nu^L \) becomes comparable with the Zeeman frequency of paramagnetic moments \( \omega_B = 1.761 \times 10^{11} \text{ s}^{-1}/T \). Such a matching of the two energy scales will disturb the intrinsic magnetic fluctuation around \( \mathbf{Q}_c \), depending on both temperature (that determines \( \nu^L \)) and the magnitude of \( B_0 \) to cause \( \omega_B \approx \nu^L \). The field-induced increase of \( \Delta K \) observed for \( \mu\text{SR} \) at lower temperatures is naturally understood by the blurring of the propagation vector \( \mathbf{Q}_c \) and associated increase of \( k^L \) that enhances \( \chi^L \) via the factor \( (Q_c/k^L)^{-2} \).

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![Schematic phase diagram displaying the quantum critical point (QCP) between metallic spin glass and Fermi liquid states along a control parameter \( \delta \). \( T_g \) is the glass temperature. Li$_{1-x}$Zn$_x$V$_2$O$_4$ is mapped onto the spin glass state, where \( 0 \leq x < 0.05 \) may correspond to the QCP \( (T_g = 0) \).](image)

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