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Muon spin relaxation measurements of LiV_2O_4

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Abstract

We report low-temperature (20 mK–5 K) muon spin relaxation (μSR) measurements of the geometrically spin-frustrated LiV_2O_4. We find that the spin dynamics of the ground state are very sensitive to magnetic impurities of the specimens. We discuss the similarities of the ground state with spin glasses.

Keywords: Muon spin relaxation; Frustration; Transition metal oxides; Heavy fermions

LiV_2O_4 is a strongly correlated (3d) electron system which is a candidate for the first-observed heavy-fermion transition-metal oxide. LiV_2O_4 is also geometrically spin-frustrated. V atoms occupy equivalent crystallographic octahedral sites of the FCC normal-spinel lattice and couple antiferromagnetically to their nearest neighbors. One V electron absorbed into a conduction band would leave a spin $\frac{1}{2}$ V network of frustrated corner-sharing tetrahedra (FCST); however, the actual situation may be more complicated than this. Previous μSR studies of FCST include the spinel Y(Sc)Mn_2 [2], and the pyrochlores $Y_2Mo_2O_7$ and $Tb_2Mo_2O_7$ [3], as well as other systems with geometric frustration such as the kagomé lattice [4]. The magnetic properties of all these systems obtained by μSR have some similarity to those of conventional spin glasses [5]. $Y_{0.97}Sc_{0.03}Mn_2$ which most closely resembles LiV_2O_4 (same structure, metallic, and a large specific heat γ-term like in heavy fermion systems) showed a distinct spin-glass-like transition whose T_g increases upon addition of impurities (Al for Mn). LiV_2O_4 is nominally a pure compound while the other compounds may necessarily be disordered, e.g., 3% Sc suppresses a structural transition at 100 K in Y(Sc)Mn_2 while no transition has been observed in LiV_2O_4 away from cubic down to 9 K. The similarities to spin glasses of these systems could be intrinsic or caused by structural defects and/or magnetic impurities. It is important to distinguish between these.

In the μSR technique (a probe of local magnetism) one measures $g_z(t)$, the averaged polarization of singly implanted muons in the sample. Different theoretical models describe its form and parameters, but in general, $g_z(t)$ depends on the internal field fluctuation rate, ν, the width, B, of the distribution of possible fields at the muon site, and the functional shape of the field distribution. We performed μSR measurements [5] in two experimental modes. In the zero applied field (ZF) mode only a local internal field ($\boldsymbol{B}$) is present. In the longitudinal field (LF) mode, an additional field, $\boldsymbol{B}_{LF}$, is applied parallel to the initial muon polarization ($\boldsymbol{\mu}_0$). For polycrystalline ZF measurements, $\frac{1}{3}\boldsymbol{\mu}_0 \| \boldsymbol{B}$ and $\frac{2}{3}\boldsymbol{\mu}_0 \perp \boldsymbol{B}$ on average. If $\boldsymbol{B}$ fluctuates slowly ($\nu \ll \gamma_\mu B$), only the transverse components of $\boldsymbol{\mu}_0$ will precess, and $g_z(t)$ will consist of two components with amplitudes of $\frac{1}{3}$ and $\frac{2}{3}$. In the paramagnetic phase ($\nu \gg \gamma_\mu \boldsymbol{B}$), $g_z(t)$ is a single component exponential.

The two samples of LiV_2O_4, we called 1 and 3, a convention from Ref. [1]. They are distinguished by their molar impurity concentrations, $n_1 = 0.03$ mol% and $n_3 = 0.15$ mol% with $S_{imp} \approx 2$ and $g_{imp} \approx 2$ [1]. Sample 3 is also slightly off-stoichiometric, $Li_{0.84}V_{1.98}O_4$.

In Sample 1 we observed no evidence of static order. The paramagnetic form, $g_z(t) = \exp(-t/T_1)$, fit the dynamic-spin relaxation data for all temperatures measured.

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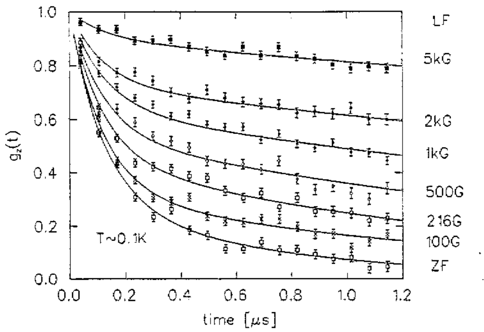

Fig. 1. Sample 3 muon polarization versus time with various applied longitudinal fields at $T = 110 \pm 15$ mK fit to $g_z(t) = A\exp(-t/T_1) + (1-A)\exp(-t/T_\perp)$.

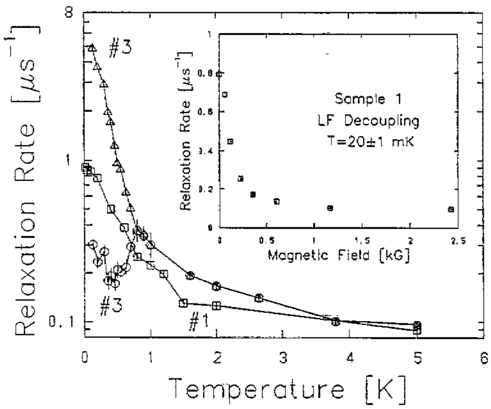

Fig. 2. μSR relaxation rate versus temperature in zero field (main figure) and versus applied longitudinal field at $T = 20 \pm 1$ mK (inset). For Sample 1 (□) represents $1/T_1$ in ZF and LF. For Sample 3 (○) represents $1/T_1$, and (△) represents $1/T_\perp$, both in ZF.

$1/T_1$ corresponds to longitudinal relaxation due to transverse dynamics. We observed no spin-glass-like transition (which would appear as a distinctive maximum in the $1/T_1$ relaxation rate) down to 20 mK. $1/T_1$ theory for $\nu \gg \gamma_\mu B$ in a LF gives $1/T_1 = 2B^2\nu/(\nu^2/\gamma_\mu^2 + B_{LF}^2)$. For Sample 1 at $T = 20 \pm 1$ mK we obtained $B_1 \sim 27$ G, $\nu_1 \sim 14\ \mu s^{-1}$, and $\nu_1/\gamma_\mu B_1 \sim 6.4$. Sample 1 remains dynamic down to 20 mK without any spin freezing.

Fig. 1 shows ZF and LF muon polarization functions at $T = 110 \pm 15$ mK of Sample 3. In ZF, there are two signal components with amplitude ratios of roughly 1 : 2. This is a signature of quasi-static order and is qualitatively different from Sample 1 which contains fewer impurities. We fit in ZF with a phenomenological form $g_z(t) = \frac{1}{3}\exp(-t/T_1) + \frac{2}{3}\exp(-t/T_\perp)$, where $1/T_\perp$ corresponds to relaxation in the transverse field components. The longitudinal $\frac{1}{3}$ component would persist at long time $(1/T_1 \to 0)$ unless some portion of $\boldsymbol{B}$ fluctuates. When $T > 0.8$ K, $1/T_1 = 1/T_\perp$ (see Fig. 2), therefore, $g_z(t)$ crosses over to the paramagnetic form.

The comparison of LF measurements of Sample 3 to Sample 1 is complicated due to the different $g_z(t)$'s in ZF. Assuming the most dynamic scenario we could force fit with formula 1. By this method we obtained at $T = 110 \pm 15$ mK, $B_3 \sim 95$ G, $\nu_3 \sim 31\ \mu s^{-1}$, and $\nu_3/\gamma_\mu B_3 \sim 3.8$. B apparently would scale with small impurity concentrations. Comparing $\nu_1/\gamma_\mu B_1$ to $\nu_3/\gamma_\mu B_3$, at roughly the same temperature, implies a slowing down in spin fluctuations in Sample 3 relative to that of Sample 1 if we expect ν to increase proportionally to the number of impurities, but a quasi-static model more reasonably takes into account the qualitative static feature of $g_z(t)$ in ZF.

When a LF is applied in the static case the average component of $\mu_0 \parallel (\boldsymbol{B}_{LF} + \boldsymbol{B})$ varies between $\frac{1}{3}$ and 1. The static and dynamic component's amplitudes become A and 1-A depending on B_{LF}/B. From the theoretical dependence of A on B_{LF}/B for dilute impurities, we estimate an internal field $B_3 \sim 250$ G. This is a factor of 2–3 more than the ZF estimation of B from the initial relaxation rate ~ 100 G. This discrepancy, "The hard to decouple effect", has been observed in other systems with spin frustration [4], and may be related to spin diffusion. The situation in Sample 3 where static and dynamic effects coexist is more complicated than in Sample 1 where dynamic effects dominate.

In the ordered antiferromagnet ZnV_2O_4 which is isostructural to LiV_2O_4, we measured B to be much larger, $B_{Zn} \sim 1.5$ kG. This is additional evidence that the relaxation in LiV_2O_4 was primarily caused by dilute magnetic impurities. The suppression of magnetism in LiV_2O_4 might be attributed to the formation of collective spin singlets, the Kondo effect, or some combination. Increasing the impurity concentration (Samples 1–3) may cause defects in these singlets, and as a result, these spins begin slowing down at a higher temperature causing increased muon spin relaxation. Sample 1 seems different from a frozen spin glass down to 20 mK. The ground state of LiV_2O_4 depends strongly on the sample stoichiometry, and the intrinsic ground state of LiV_2O_4 can only be extrapolated because we lack an ideal sample. From the behavior of Samples 1 and 3, we can expect that an ideal sample of LiV_2O_4 would show no magnetic freezing/order.

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