# Magnetic correlations in frustrated LiV2O4 and ZnV2O4

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# Magnetic correlations in frustrated $LiV_2O_4$ and $ZnV_2O_4$ ☆

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In the $AB_2O_4$ normal spinel structure, the B ions form a sublattice of corner sharing tetrahedra while each B ion is octahedrally coordinated by six oxygens. For an ideal tetrahedral lattice of V spins on the B site in $(Li{:}Zn)V_2O_4$ combined with simple antiferromagnetic (AFM) next-nearest neighbor interactions, a highly frustrated magnetic state results. The characteristic feature of this *geometric* frustration is the absence of long-range (Néel) order, in contrast to canonical spin glasses where frustration is caused by site disorder [1]. It has been pointed out [2] that in the cubic spinels canonical spin-glass behavior is unlikely. $LiV_2O_4$ gained additional interest after reports of heavy-fermion (HF) formation at low temperatures [3], making it a d-based HF system. The role of geometric frustration in connection with Fermi-liquid behavior is discussed in Refs. [4,5]. Heavy-quasiparticle excitations originating from Heisenberg rings with $S = \frac{1}{2}$ and chains with $S = 1$ have been calculated in Ref. [6]. Quasielastic neutron scattering showed that at higher temperatures the relaxation rates increase linearly on momentum transfer typical of ferromagnetic spin-fluctuation systems [7]. Below 40 K, AFM fluctuations dominate and the relaxation depends only weakly on momentum transfer.

Fig. 1 presents the temperature dependence of the spin–lattice relaxation of $LiV_2O_4$ at different frequencies and external fields. At low frequencies a cusp-shaped maximum appears at $\sim 0.6$ K which becomes suppressed at higher frequencies and fields. Below 2 K the anomalous temperature dependence of $1/T_1$ is strongly dependent on frequency and the nuclear relaxation is markedly enhanced at low frequencies. These are similar characteristics as seen for the Li nuclear relaxation in Li doped CuO and NiO [8]. Those results have been compared to the spin dynamics in cuprate superconductors. Based on this interpretation the cusp-like anomalies in Fig. 1 are due to an exponentially decreasing magnetic relaxation rate $\Gamma = \Gamma_0 \exp(-\Delta/k_B T)$ indicating the slowing down of spin fluctuations on the NMR time scale. The corresponding

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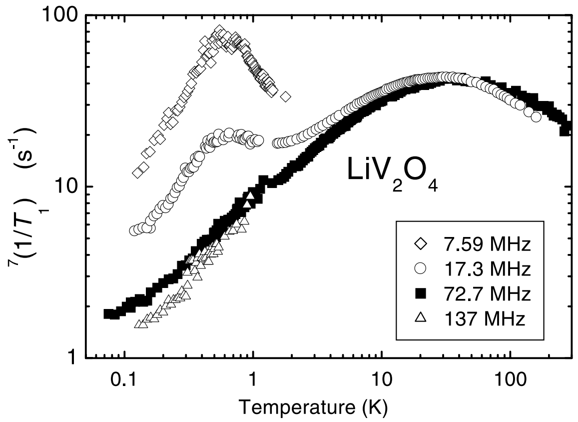


Fig. 1. $^7$Li NMR spin–lattice relaxation rate $\log(1/T_1)$ vs. $\log T$ in $LiV_2O_4$ measured at different frequencies/applied fields.

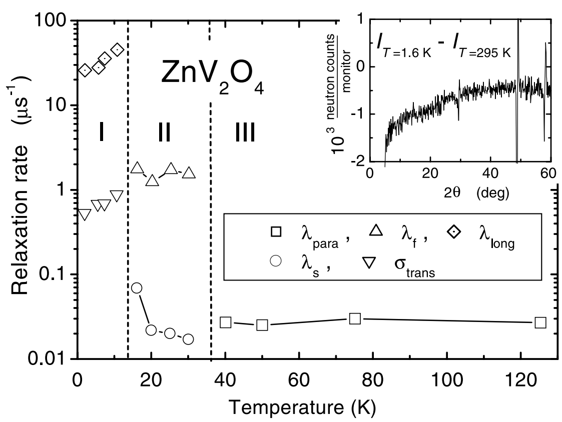


Fig. 2. μSR rates as a function of temperature in $ZnV_2O_4$. The meaning of the labels are explained in text. Inset: difference spectrum from neutron diffraction.

slowing down of $1/T_1$ is driven by a characteristic energy $\Delta$ of the order of 1 K. This energy reflects probably an average barrier between neighboring configurations of a highly degenerate ground state. Alternatively, the effective interaction energy $\Delta$ could be caused by dynamic singlet pairing leading to an interpretation along the model of a 'cooperative paramagnet' proposed in Ref. [2]. The persistence of slow spin dynamics was also observed in a μSR study [9] down to 20 mK. The μSR rate of the $LiV_2O_4$ sample with the lowest impurity concentration showed on cooling only a slowing down of spin fluctuations, with no indication of static spin freezing. We point out that these μSR results combined with the absence of a static quadrupolar splitting in the $^7$Li NMR spectra [10] give strong evidence that the spin–lattice relaxation process in our NMR data is not driven by the interaction of dynamic electric field gradients with the $^7$Li quadrupole moment.

In $ZnV_2O_4$ a cubic to tetragonal phase transition occurs around 50 K [11] which is claimed to remove the geometric frustration. This was supported by an earlier neutron diffraction (ND) study reporting AFM order below 45 K [12]. A new experiment with the aim to verify the results of [12] showed no well defined magnetic Bragg peaks (see inset in Fig. 2) and the data were compatible with short-range magnetic order at best. This initiated the μSR study in order to clarify the situation. The measurements were carried out at the M20 surface muon facility of TRIUMF. From the shape of the zero field (ZF) spectra one can distinguish three magnetic regions, labeled III, II, I in order of descending temperature as it is shown in Fig. 2. In region III ($T > 40$ K), the muon spin relaxes exponentially with a very low and temperature independent rate $\lambda_{\rm para}$ which is typical of a well-established paramagnetic state where uncorrelated spins fluctuate rapidly. In region II ($10\ {\rm K} < T < 40$ K) two magnetic states coexists: The paramagnetic state with slow relaxation rates $\lambda_{\rm s}$ together with a dynamically correlated spin-glass-like state characterized by fast exponential relaxation rates $\lambda_{\rm f}$. The fast rate is barely affected by a longitudinally (i.e. in muon spin direction) applied field of 3 kOe proving that the latter state is far away from spin freezing. The relative volume fraction of this state increases continuously on cooling. A similar magnetic regime was detected by μSR in other geometrically frustrated compounds, as $YMn_2$ and related intermetallics [13]. The rate $\lambda_{\rm s}$ increases on cooling toward 10 K, showing the typical critical slowing down of paramagnetic spin fluctuations on approach to a magnetic transition. No such effect is seen in region III, meaning that 40 K is not a magnetic phase transition point. In region I ($T \leqslant 10$ K), the observed μSR signal is of the form $A(t) = (a_0/3)\{2J_0(\omega_\mu t)\exp[-\sigma_{\rm trans}^2 t^2] + \exp[-\lambda_{\rm long} t]\}$ with $J_0$ being the zero-order Bessel function and $\omega_\mu$ the muon spin precession frequency. The two terms are the transverse and the longitudinal signal of an ordered magnetic powder sample. The Bessel-type oscillations are the result of the special distribution of the field at the muon site in an incommensurate spin density wave (ISDW). The presence of the additional Gaussian damping term indicates an additional source of field distribution such as local random spin disorder in the ISDW structure. Fig. 2 shows the rate $\sigma_{\rm trans}$ to be very large. The local spin disorder must be substantial, preventing true long-range correlations in the ISDW state. This explains our ND result. The longitudinal rate $\lambda_{\rm long}$ is the response to slow spin fluctuations (i.e. within the μSR time window of MHz to GHz) in an ordered state. Fig. 2 demonstrates that these spin fluctuations persists to low temperatures and that the system never reaches the quasi-static limit characteristic for typical ferro- or antiferromagnets. The persistent spin fluctuations, which tie in with the results for $LiV_2O_4$, the substantial local spin disorder, which prevents the formation of a fully long-range correlated magnetic ground state, and the occurrence of a dynamic spin-glass-like magnetic precursor state are all indications for the presence of geometric frustration. The tetragonal lattice distortion in $ZnV_2O_4$ removes some, but not all, frustration. The partial removal of frustration allows the formation of a medium-range correlated magnetic ground state, in contrast to the situation in $LiV_2O_4$.

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