μSR Study of a Quantum Spin Liquid Candidate : the S=1/2 vanadium Oxyfluoride kagome Antiferromagnet

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Abstract. We present a detailed μSR study of the recently synthesized compound, $[NH_4]_2[C_7H_{14}N][V_7O_6F_{18}]$ (DQVOF), a geometrically frustrated magnetic material, both in longitudinal and transverse configurations. The μSR measurements in zero and longitudinal field show that there is no spin freezing down to 20 mK which is the key requirement for a quantum spin liquid state. Further experiments in transverse field single out two contributions with different shift and broadening which shed a new light on the location of the muons stopping sites.

Understanding quantum spin liquid states (QSL) such as the resonating valence bond state (RVB) formed by macroscopic resonance between the various spin singlet coverings of the lattice, has been a long standing issue in condensed matter research [1, 2, 3, 4]. In two dimensions, the search for such states has focused on the S=1/2 quantum kagome antiferromagnet (QKAFM), which features a highly frustrated lattice of corner sharing equilateral triangles. Among the rare experimental candidates for a QKAFM, the recently synthesized $[NH_4]_2[C_7H_{14}N][V_7O_6F_{18}]$ (DQVOF) compound [5] is the first one based on V^{4+} (d^1) ions rather than the more usual Cu^{2+} (d^9) ions [6, 7, 8, 9], thus allowing the investigation of the effects of different perturbations to the ideal Heisenberg Hamiltonian.

The DQVOF material exhibits a rather complex bi-kagome layer structure (see figure 1 c)). It contains two different types of vanadium ions; V^{4+} S=1/2 ions forming the kagome layers and additional V^{3+} S=1 ions forming a triangular layer in between the kagome ones. These kagome bi-layers are well separated from each other by large organic molecules [5]. Previous low temperature heat capacity, susceptibility and magnetization measurements showed that the V^{3+} ions are very weakly coupled to the V^{4+} kagome layers so that the material is a good candidate to investigate the physics of the QKAFM [10]. From heat capacity analysis, the system shows a gapless behavior down to at least 350 mK with an original T-linear behavior

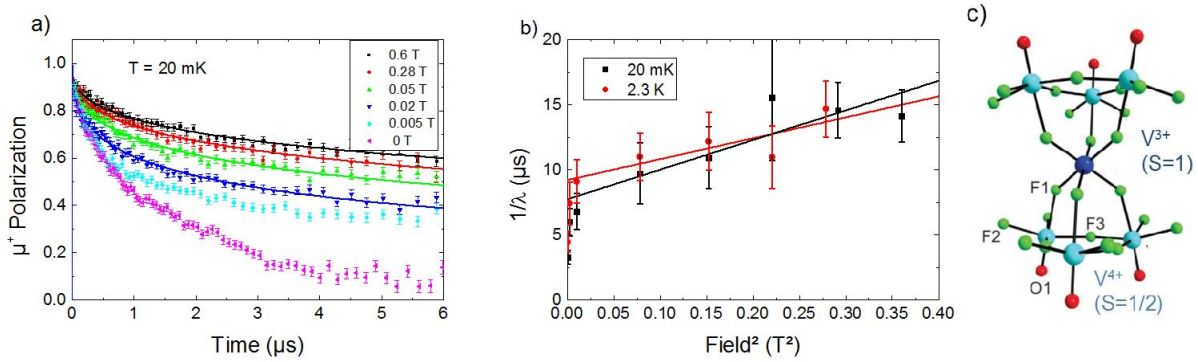

Figure 1. a) Time dependent muon spin polarization in DQVOF at 20 mK with different applied longitudinal fields. Solid lines are fits to the data. b) Inverse of the relaxation rate versus field square. Solid lines are fits to the data. c) Local structure of the compound.

suggesting fermionic excitations. μSR experiments in zero and low longitudinal field [10] have clearly demonstrated the absence of any spin freezing down to at least 40 mK. Further, these measurements have evidenced a slowing down of the spin dynamics below about 10 K and down to 1 K where the muon relaxation rate reaches a dynamical plateau as often observed in highly frustrated magnets. In such a complex system featuring strongly correlated quantum spins together with nearly free S=1 spins, asserting the origin of the spin dynamics remains a challenging problem. In this proceeding we present further μSR experiments on this compound. Zero field measurements which demonstrates the absence of spin freezing down to 20 mK and longitudinal and transverse field experiments which allow to characterize the evolution of the spin dynamics at low temperature and clarify the role of both types of vanadium spin on the muon relaxation.

The experiments were performed on a DQVOF powder sample synthesized as explained in [5]. The measurements were performed on the GPS and the LTF spectrometers at the Laboratory for Muon Spin Spectroscopy at the Paul Scherrer Institute. For the GPS experiment, we used 300 mg of sample wrapped in a thin aluminium foil inserted in a He-flow cryostat to vary the temperature in the range 1.6 K-200 K. The sample was first measured in a background free configuration and then mounted on a standard silver sample holder. Within our accuracy, we could not detect any fraction of signal arising from muons falling in the silver sample holder. Therefore we used the latter setup for all the measurements in longitudinal and transverse configurations. For the LTF experiment, where the temperature varies from 2.3 K down to 20 mK, about 200 mg of sample powder was deposited on a silver plate and then fixed using diluted varnish. By comparison to the GPS experiment we estimated the background asymmetry corresponding to muons falling in the LTF sample holder to be ~ 0.021.

From the analysis performed in [10], the relaxation of the muon polarization in zero field consists of three different contributions; about 10% of the muons strongly couple to the fluorine ions to form a F-μ-F complex, another minor fraction of muons ($\sim$ 10 %) stop far from the kagome planes, likely in the organic molecule in between the magnetic layers, and most of the muons ($\sim$ 80 %) stop near the oxygen ions, close to the V^{4+} kagome planes. The two minor fractions can be decoupled easily by applying a longitudinal field of 0.02 T. As a consequence, following Ref.[10], we analyze the data obtained by applying longitudinal fields larger than 0.02 T to track the dynamical electronic contribution in isolation. The sizable relaxation observed at 20 mK even under the strongest 0.6 T applied field, see figure 1 a), leaves no doubt on the

dynamical character of the relaxation. This extends down to 20 mK, the conclusion of Ref. [10] that DQVOF possesses a dynamical ground state.

We fitted the relaxation measured with an applied longitudinal field larger than 0.02 T to a stretched exponential

$$P(t) = exp(-\lambda t)^{\beta} + B \tag{1}$$

where λ is the muon depolarization rate, β is the stretched exponent and B accounts for the fraction of muons fully decoupled in fields stronger than 0.02 T. The two latter parameters were fixed to the values obtained by fitting the 0.02 T field data, namely β=0.48 and B=0.35 at T=20 mK, and β=0.51 and B=0.35 at T=2.3 K in the crossover regime where the spin dynamics slows down drastically. The variation as a function of the applied field of the only free parameter λ is very similar at the two studied temperatures, see figure 1 b). Coming from low fields, the relaxation time $1/\lambda$ first increases rather rapidly with the applied field up to H $\sim$ 0.1 T, before showing a weaker field dependence which can be approximated by a H^2 variation. Although the initial increase is poorly understood, the higher field regime suggests an analysis within the Bloembergen Purcell and Pound (BPP) theory which predicts for a simple spin dynamics $\langle S(t)S(0)\rangle \propto \exp(-\nu t)$

$$\lambda = \frac{2\gamma_\mu^2 H_{Fluc}^2 \nu}{\nu^2 + \gamma_\mu^2 H_{LF}^2} \tag{2}$$

where γ_μ is the muon gyromagnetic ratio, H_{Fluc} is the internal fluctuating field, ν is the fluctuating frequency and H_{LF} is the longitudinal applied field. Within this model, one can calculate the fluctuating field and frequency for each temperature. We find H_{Fluc}=0.007(1) T and ν=470(80) MHz, and H_{Fluc}=0.007(1) T and ν=620(125) MHz respectively at T=20 mK and T=2.3 K. This represents a drastic slowing down as compared to both V^{3+} and V^{4+} estimated fluctuation frequencies in the paramagnetic limit, respectively ν^{3+}=523 GHz and ν^{4+}=13.337 THz.

To gain a better understanding of the local magnetic properties, we performed transverse field experiments at different temperatures. For all the experiments we used a transverse field of 0.5 T. On the GPS experiment, the field is created by a resistive magnet powered by a stable power supply. In order to determine accurately the shift reference, we measured the signal from a bare silver plate at 60 K and assumed that the field remained constant during whole experiment. On the LTF spectrometer, the field is produced by a superconducting magnet used in persistent mode. The sizable fraction of muons falling in the silver sample holder used in this experiment allowed us to determine the shift reference. For the analysis, the relaxations were transformed into a rotating reference frame at 70 MHz (RRF), about 2.5 MHz higher than the free muons rotation frequency at 0.5 T.

Although the relaxations were fitted in the time domain, the general evolution versus temperature is clearer on the Fourier transforms shown in figure 2 a) and 3 b). In the GPS experiment, the signal at high temperature consists of two different peaks, one narrow which remains clearly visible down to 2.3 K and one additional peak which broadens drastically upon cooling and eventually becomes too broad below 10 K to be detected. At low temperatures, in the LTF experiment the Fourier transforms consist of two peaks, one narrow and one broader (see figure 3 b)). There, the narrow peak corresponds to the silver background while the broad peak is the sample signal, inline with the GPS low temperature results.

In order to extract the shift and the depolarization rate of each components, we fitted the time dependent relaxations at each temperature. From 200 K to 10 K, given that two components, a gaussian and a lorentzian, are clearly seen in the Fourier transform spectra, we fitted the relaxations to two oscillations with different broadenings :

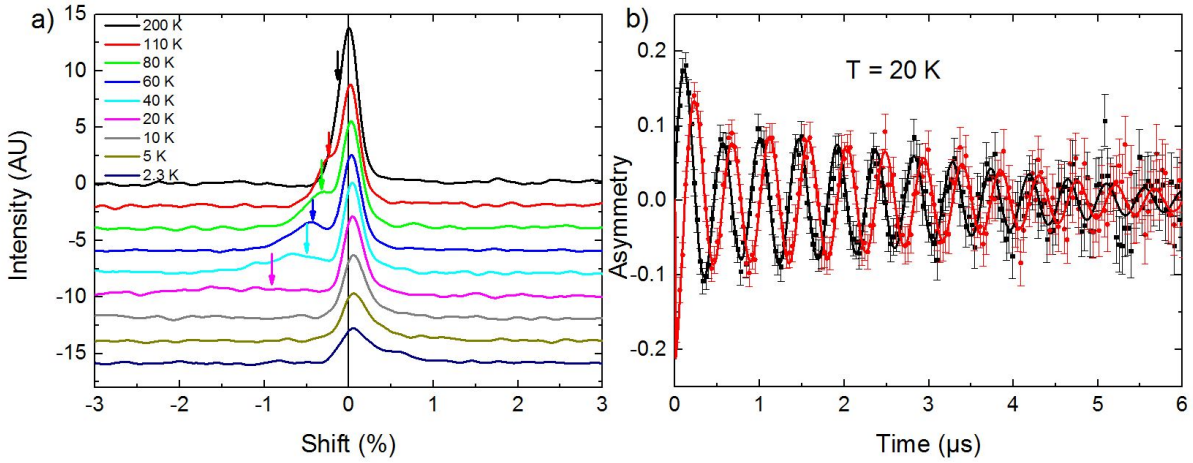

Figure 2. a) Fourier transforms of the asymmetries at different temperature with an applied transverse field of 0.5 T versus shift. The arrows are showing the broad peak center. The datas were taken on the GPS spectrometer. b) Time dependent signal at 20 K. Solid lines are fit to the data.

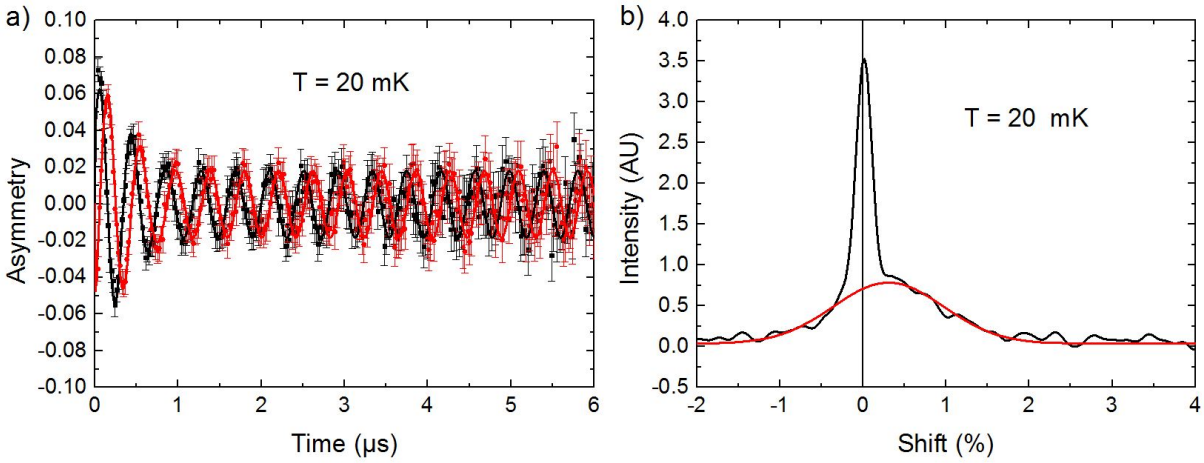

Figure 3. a) Time dependent signal at 20 mK with an applied transverse field of 0.5 T. Solid lines are fit to the data. b) Fourier transform of the signal. The red line is a fit of the broad peak hidden under the silver narrow peak. The datas were taken on the LTF spectrometer

$$A(t) = A_1 cos(2\pi\nu_1 t + \phi_1) e^{(-\lambda_1 t)^2} + A_2 cos(2\pi\nu_2 t + \phi_2) e^{-\lambda_2 t} \quad (3)$$

where ν_i are the oscillation frequencies, ϕ_i their phases, A_i their initial asymmetries and λ_i their depolarization rates. We fixed the different A_i to the values found at 20 K, A_1=0.099 and A_2=0.129. Below 10 K we fitted the data only after 0.1 μs keeping only the first oscillation in formula 3.

In the LTF experiment, we still used equation (3) to fit the time domain relaxation in the RRF, ignoring the initial fast relaxation as below 10 K in GPS. Here the second oscillation

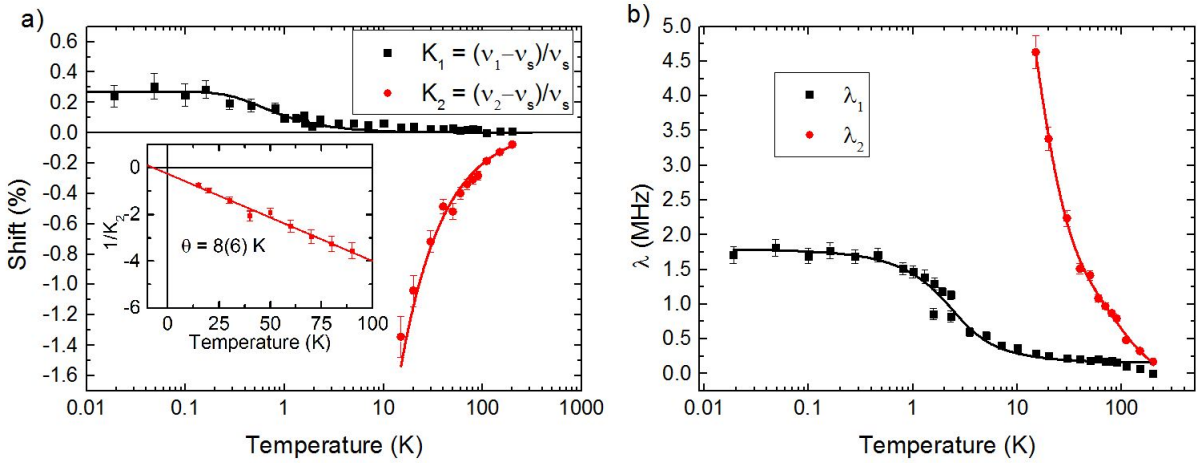

Figure 4. a) Shift versus temperature. K_1 relates to the narrow peak at high temperature and K_2 to the broad one. Inset : $1/K_2$ versus temperature. Solid lines are fits to the data. b) Depolarization rate versus temperature. λ_1 is relative to the narrow peak at high temperature and λ_2 to the broad one. Solid lines are guides to the eyes.

accounts for the hardly relaxing silver background and hence we fixed λ_2=0. The remaining parameters A_1=0.040, A_2=0.016 and ν_2=2.43 MHz (in the rotating reference frame) were kept constant over the investigated 20 mK-2.3 K temperature range.

The results of all fits are reported in figure 4. We defined the shift as $K_i = (\nu_i - \nu_s)/\nu_s$ where ν_s is the rotation frequency in silver. As one can see in figure 4 a) K_1 is increasing below about 5 K and saturates at a value of $\sim$ 0.27 % below 100 mK. The lines in the main panel of figure 4 a) are fits of the shift to a pure S=1 Brillouin function where the only free parameter is the amplitude. Similarly, as shown in figure 4 b) the depolarization rate related to the muons referenced as 1 also saturates below 100 mK. This leads us to believe that they are mainly influenced by the vanadium V^{3+} ions (S=1) which are in between the kagome layers and hence track their susceptibility. Due to the low value of the saturating shift, the muons are likely stopping in the material far from the V^{3+}, i.e. near the kagome planes. The shift at the second muon site can be fitted to a paramagnetic Curie-Weiss law with a small θ=8(6) K, which reminds also the magnetic behavior of the interlayer V^{3+} ions. Therefore, the muons referenced as 2 seem also mainly influenced by the nearly free V^{3+}. The small coupling θ between the V^{3+} interlayer ions is consistent with the coupling ($\sim$1 K) found in [10] by analyzing the specific heat and magnetization data. From the amplitude of the Curie like law in the inset of figure 4 a) we estimate the average distance from the muons corresponding to the second signal to the vanadium V^{3+} to be r_{max}=2.4(1) $\mathring{A}$. This locates them quite near the interlayer vanadium. Finally, those transverse field experiments suggest that the muons are experiencing a predominant influence from the interlayer vanadium (S=1) and allow the identification of two different muons sites that were not separated in the longitudinal field relaxation. Given the nearly similar values of A_1 and A_2, it is tempting to assign the corresponding signals to muons stopping near the two different triangles which constitute the kagome planes of DQVOF [5]. One kind of triangles is located above and below V^{3+} ions as shown in figure 1 c). Muons stopping close to those triangles strongly feel the V^{3+} dipolar field. The other kind of triangles made of V^{4+} coupled by the $F2$ fluorine anions are not bridged by the V^{3+} ions and the muons stopping nearby should feel a weaker dipolar field.

In summary, this μSR study shows that there is no spin freezing down to 20 mK in DQVOF and that the muons are preferentially implanted in two different sites in the material. First the longitudinal field experiments leave no doubt about the dynamical nature of the relaxation down to 20 mK. Furthermore, the low values of the fluctuating fields and frequencies at 20 mK and 2.3 K tend to prove that the dynamical behavior of the compound can not be simply understood in the paramagnetic limit of neither V^{3+} nor V^{4+} ions. It should arise from the existence of strong correlations in the low temperature phase of this highly frustrated compound. Second, the transverse field experiments clearly show that the signal consists of two main contributions. The analysis of the shifts suggests that they are related to the two different kind of triangles forming the kagome planes of DQVOF.

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