Dynamics in pure and substituted volborthite kagome-like compounds

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Abstract

Volborthite Cu\textsubscript{3}V\textsubscript{2}O\textsubscript{7}(OH)\textsubscript{2} \cdot 2H\textsubscript{2}O is a natural frustrated antiferromagnet with a kagomé-like magnetic lattice decorated by $S = \frac{1}{2}$ spins. Our $\mu$SR results confirm the existence of a dynamical plateau below 2 K, as initially demonstrated in [Phys. Rev. Lett. 91 (2003) 207603] despite sensible quantitative differences in the relaxation rate values. Thanks to additional low temperature SQUID and NMR data we show that this plateau occurs concurrently with a freezing transition. Moreover, we revisited the effect of diluting the magnetic lattice for small dilution rates between 1% and 15%. Comparison is made with the well studied kagomé bilayer compounds. The ground state of volborthite appears to be far less stable with respect to dilution.

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In the field of frustrated antiferromagnets, the recently rediscovered volborthite Cu\textsubscript{3}V\textsubscript{2}O\textsubscript{7}(OH)\textsubscript{2} \cdot 2H\textsubscript{2}O \cite{1,2} plays a special role as it approaches the theoretical model of quantum spins $S = \frac{1}{2}$ on the highly frustrated kagomé lattice. For such a spin system, the ground state is expected to be of liquid type, with short range correlations and persisting dynamics at $T \rightarrow 0$ \cite{3,4}.

Seminal muon spin relaxation experiments demonstrated the existence of persisting dynamics in the archetypal Cr\textsuperscript{3+} ($S = \frac{3}{2}$) kagomé bilayers SrCr\textsubscript{9}Ga\textsubscript{12}–\textsubscript{9}pO\textsubscript{19} (SCGO) \cite{5} and Ba\textsubscript{2}Sn\textsubscript{2}ZnGa\textsubscript{10}–\textsubscript{7}pCr\textsubscript{7}pO\textsubscript{22} \cite{6} ($p < 0.97$) or the Cr\textsuperscript{3+} jarosite compounds \cite{7}. However direct comparison to theoretical calculation still claims for a closer experimental realization of the theoretical model. Moreover understanding the interplay between the persistent dynamics observed in $\mu$SR and the concurrent freezing observed at low-$T$ in susceptibility measurements in the archetypal frustrated magnets \cite{8} remains a pending question and certainly deserves further theoretical and experimental investigations on new systems.

Volborthite consists of CuO layers well separated from each other by V\textsubscript{2}O\textsubscript{7} pillars and water molecules. In this compound, Cu\textsuperscript{2+} ($S = \frac{1}{2}$) are the only magnetic atoms and they form planes of corner-sharing triangles. The resulting magnetic structure is a stacking of well separated (7.2 Å) kagomé-like lattices fully covered by $S = \frac{1}{2}$ spins. Due to a small monoclinic distortion, there might exist two Cu–Cu interaction constants, i.e. the kagomé lattice is built on isosceles triangles rather than equilateral ones. Whether this possible dissymmetry of the exchange paths impacts the nature of the ground state (GS) is still an open question and certainly requires refined calculation. On experimental grounds, a former $\mu$SR study \cite{9} evidenced a slowing down of spin fluctuations below 5 K followed by nearly temperature independent fluctuations below 1.5 K and down to 50 mK, demonstrating the liquid nature of the GS. The lowest temperature of former SQUID, heat...
capacity and NMR experiments [2] was 1.8 K and could not conclude on the nature of the low-\(T\) regime exhibited in \(\mu\)SR, in particular no magnetic transition was found above 1.8 K. In order to investigate this low energy regime, as compared to the exchange energy \(J \approx 90\) K [2], we performed low-\(T\) SQUID, NMR and \(\mu\)SR experiments on the pure compound. Besides, we investigated through \(\mu\)SR and SQUID measurements the effect of diluting the magnetic network of volborthite in Zn \((S = 0)\) substituted samples.

The macroscopic susceptibility of pure volborthite is presented in Fig. 1. At high temperature, the behavior is of the Curie–Weiss type with \(\theta_0 \approx 130\) K but due to frustration no transition in the magnetic susceptibility is detected at this mean field temperature. The bump at around 25 K probably reflects the development of short range spin correlation at this temperature [2,10]. Below 2 K the separation of the zero field cooled (ZFC) and field cooled (FC) magnetization signals a freezing process. Below 2 K, the ZFC branch shows a very broad maximum at around 1.3 K which probably arises from a rather large distribution of freezing temperatures as confirmed by NMR data [11].

Fig. 2 shows the muon relaxation rate in volborthite measured in a 100 G longitudinal applied field to decouple the nuclear dipoles. It appeared that the time dependence of the asymmetry cannot be fitted by a simple functional form on the whole time scale. The relaxation rates were estimated by taking into account the \(1/e\) decay time. As in Ref. [9], we find that the spin dynamics slow down below 5 K and reach a dynamical plateau below 2 K. Despite qualitative agreement, the relaxation rate we measured appears to be 14 times larger than the one reported in Ref. [9]. Since defects in the magnetic structure reduce drastically the \(T \to 0\) relaxation rate (see discussion on the Zn substituted sample), one possibility is that our samples are slightly better crystallized as a result of a slightly different synthesis protocol (see details of preparation in Ref. [11]).

For comparison, we also plotted in Fig. 2 the vanadium nuclear spin lattice relaxation rate \(1/T^\text{NMR}_1\) measured by pulsed NMR. Contrary to the muon relaxation rate, the latter decreases below the transition observed in the SQUID experiment, as expected for a frozen ground state. Moreover, if we assume that the field at the muon site is \(H_A \approx 35 G\) as in Ref. [9], from the muon relaxation we measured, we get 3.5 \(\mu\)s\(^{-1}\) for the copper electronic spin fluctuations. From this value and the vanadium hyperfine coupling value \(A = 7.7\) kOe, we would expect to get \(1/T^\text{NMR} \approx 20\) ms\(^{-1}\), two orders of magnitude larger than what we measured. This suggests that the electronic spin fluctuations which are efficiently probed in \(\mu\)SR experiments are somehow filtered out at the vanadium nuclear site. Actually, the vanadium position in the unit cell is quite specific since it lays at the center of the hexagons of the kagomé lattice. Therefore for some very specific spin configurations and specific correlated fluctuations of the spins belonging to a same hexagon, it is possible that vanadium nuclei indeed only feel a static resulting field [11]. On the other hand, muons, which probably sit near oxygens, at non-symmetric sites, do not present this filtering effect.

In order to test the stability of the volborthite ground state with respect to dilution and to compare with the SCGO kagomé bilayer archetype, it is possible to substitute \(\text{Zn}^{2+} (S = 0)\) at the \(\text{Cu}^{2+}\) site with no major distortion of the lattice. Decoupling experiment at base temperature in a 2.5 % at. Zn/Cu substituted sample is shown in Fig. 3. A small applied field of 65 G decouples the nuclear dipoles. Then for increasing fields, the decoupling is much less efficient. Asymmetry is not fully restored in a 1600 G field whereas the internal field at the muon site is of the order of 35 G as mentioned before [9]. Therefore the ground state in the substituted samples remains dynamical as for the pure

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**Fig. 1.** Macroscopic susceptibility versus temperature in pure volborthite in 100 Oe. Inset: zoom on the very low temperature data. The upturn below \(T \approx 200\) mK is an artifact due to few ppm magnetic impurities in the grease used to ensure thermalization of the powder sample.

**Fig. 2.** Comparison of the \(T\) dependence of the muon relaxation rate (left axis) and \(^{51}\text{V}\) nuclei relaxation rate in pure volborthite.
compound, at least for small dilution rates. It is however noticeable that the relaxation rate at base temperature in this substituted sample \( \lambda \approx 1 \mu s^{-1} \) is nearly five times smaller than in the pure sample. Such a decrease of the relaxation rate on the dynamical plateau upon dilution was reported for kagomé bilayer [7,6] as well as for volborthite [9]. However, the decrease reported in Ref. [9] was only a factor 1.5 from the pure compound to the 5% Zn substituted sample. To refine the more drastic effect of dilution we observed here, we studied systematically \( \left( \text{Cu}_{1-x} \text{Zn}_x \right) \text{V}_2 \text{O}_7 \cdot \text{OH} \cdot 2\text{H}_2\text{O} \) samples for smaller dilution rates \( x = 0.01, 0.025, 0.05, 0.1 \) and 0.15 than in Ref. [9].

For all samples we found a low-\( T \) dynamical plateau feature and the values of the relaxation rates on the plateau are presented in Fig. 4 as a function of the magnetic lattice covering. In comparison to the SCGO case, we find a much stronger effect of dilution we observed here, we studied systematically \( \left( \text{Cu}_{1-x} \text{Zn}_x \right) \text{V}_2 \text{O}_7 \cdot \text{OH} \cdot 2\text{H}_2\text{O} \) samples for smaller dilution rates \( x = 0.01, 0.025, 0.05, 0.1 \) and 0.15 than in Ref. [9].

In order to investigate further this dilution effect, we also performed low-\( T \) SQUID measurements on two substituted samples with 2.5% and 5% dilution rate respectively. Like the pure compound, both present a rather broad transition at low-\( T \) and we defined the transition temperature as the temperature of the maximum on the ZFC branch. The transition temperatures are shown in the bottom panel of Fig. 4 as a function of dilution and compared to SCGO compounds. Here again we find a much larger influence of dilution on the transition temperature than in SCGO. The simultaneous occurrence of the transition to a frozen state and the dynamical plateau observed in \( \mu \)SR in addition to the similar drastic effect of dilution on both the relaxation rate on the plateau and the transition temperature suggest a deep link between these two physical observations. Both seem to be manifestations of one original ground state.

In conclusion, with \( \mu \)SR, NMR and low-\( T \) SQUID experiments, we established that volborthite undergoes a transition to an original, partially frozen, state that still retains spin fluctuations. As a rather simple system, volborthite certainly opens route for close comparison to theoretical approaches.

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