In the quest for novel states of condensed matter, frustration has emerged as a key concept. In magnetic systems, competitive interactions resulting from the geometry of the lattice, especially for corner sharing networks, can lead to a macroscopic entropy at T=0 K and could favor a novel spin liquid state. Theoretically, Heisenberg S=1/2 antiferromagnet on a 2D kagome lattice is predicted to lead to such an exotic quantum state. Actually very few real systems approach this model. So far, the Cr$^{3+}$(S=3/2) kagome bilayer compounds SrCr$_9$Ga$_{12}$-9$_p$O$_{19}$ (SCGO) and Ba$_2$Sn$_2$ZnGa$_{10}$-7$_p$Cr$_7$O$_{22}$ ($p<0.97$) have been the experimental archetypes of Heisenberg frustrated antiferromagnets. In this context, the recent rediscovery of Volborthite Cu$_3$V$_2$O$_7$(OH)$_2$•2H$_2$O is a major step towards a realization of the theoretical model. The magnetic lattice of this natural antiferromagnet consists of quantum S=1/2 (Cu$^{2+}$) spins sitting at the vertices of well separated (7.2Å) kagome-like planes. The lattice displays a monoclinic distortion, possibly yielding two Cu-Cu interaction constants $J_1 \neq J_2$, which does not seem to impact on the characteristic fingerprints of frustration. Indeed, despite strong antiferromagnetic interactions ($J \simeq 90$ K), no transition towards an ordered state has been detected down to 1.8 K, neither in susceptibility nor in heat capacity measurements. Instead, a maximum in both these quantities is observed around 20 K, probably reflecting the enhancement of short range correlations, and defines a new low energy scale as a result of frustration. Besides, as in kagome bilayers, muon spin relaxation ($\mu$SR) experiments detected no sign of static spin freezing but rather temperature independent spin fluctuations persisting down to 50 mK, indicative of a fluctuating quantum GS. Only in one ESR study the existence of an internal field was evidenced at 1.8 K which was interpreted as short range order.

In this Letter, we show, for the first time, that volborthite undergoes, around 1.3 K, a transition to a frozen state which we characterize using $^{51}$V NMR as a local probe of magnetism. Note that, so far, NMR investigations of the GS in the kagome bilayers had proved to be impossible because of a wipe out of the NMR intensity at low T. The volborthite powder samples were prepared by refluxing an aqueous suspension of V$_2$O$_5$ and a basic copper (II) carbonate salt Cu(OH)2-Cu(CO$_3$) for several days. No spurious phase was detected in X-ray measurements. SQUID and NMR measurements above 2 K and $\mu$SR experiments on these samples were similar to the above described published data.

The low T static susceptibility of volborthite is presented in Fig. (top panel). Below 2 K, the separation between the field cooled (FC) and zero field cooled (ZFC) susceptibilities reveals a spin freezing process. At 1.2 K, "ageing" effects have been observed (not shown here) which ascertains the glassy nature of the GS. At variance with textbook spin glass transition, the FC susceptibility does not level off below the transition and the hardly detectable broad maximum on the ZFC branch occurs below the FC/ZFC separation. This suggests a rather broad distribution of freezing temperatures as, for instance, in super-paramagnets where spin clusters get progressively blocked on lowering T.

To address the important issue of the intrinsic character of this glassy low-T phase, the susceptibility of two zinc substituted samples is also reproduced in Fig. Zn atoms enter Volborthite lattice without noticeable distortion. Since Zn$^{2+}$ is non-magnetic, the Zn/Cu substitution results in diluting the kagome magnetic lattice. The freezing temperature $T_g$ defined here as the temperature of the ZFC maxima, are plotted in the inset of Fig. as a function of the magnetic lattice dilution and compared to the same data for SCGO compounds. In marked contrast with SCGO, $T_g$ for Volborthite is strongly affected by dilution. This reminds us of the drastic reduction upon dilution of the dynamical plateau value seen in $\mu$SR experiments and suggests that the bilayer topology
likely better accommodates defects than the single layer one in volborthite. Nonetheless, in both systems, the random dilution of the magnetic network reduces $T_g$ and hence simple magnetic dilution as a source of disorder cannot explain, alone, the spin-glass like transition.

Microscopic insight into this ground state is provided by our low-T $^{51}$V NMR experiments. The non-magnetic $V^{5+}$ ions are situated above or below the center of the stars which constitutes the kagomé lattice. They thus probe symmetrically the magnetism of six $Cu^{2+}$ ions belonging to the same hexagon through an hyperfine coupling, estimated to be $A \approx 7.7$ kOe from susceptibility versus NMR shift measurements (see Ref. [12]) above 90 K in agreement with the value estimated in Ref. [4].

The nuclear spin lattice relaxation has been measured by the saturation-recovery method and fitted to a sum, with T-independent coefficients, of four exponential terms with relaxation rates proportional to $1/T$, as expected for a S=7/2 nuclear spin [14] in the case of partial saturation of the NMR line. The divergence of $1/T_1$ at 1.4 K±0.2 K (Fig. 3 inset) is a strong evidence that the vanadium probe indeed feels a transition in agreement with our susceptibility measurements. Following the analysis of Ref. [3] of the zero field $\mu$SR relaxation rate below 1 K ($\lambda = 5 \text{ ms}^{-1}$ in our sample [12]), we get 3.5 MHz for the copper spin fluctuation rate. From the hyperfine coupling $A$, we would then expect the corresponding $^{51}$V $1/T_1$ to be $\approx 20 \text{ ms}^{-1}$, much higher than the value actually measured. This suggests that spin fluctuations, seen in $\mu$SR, are efficiently filtered by the nuclear probe. We shall come back to this point later.

Characteristic $^{51}$V ($\gamma/2\pi = 11.1923 \text{ MHz/T}$) NMR spectra measured at $\nu_0 = 20.733 \text{ MHz}$, below 5 K, are presented in Fig. 2. At these low T, the quadrupolar splitting of the S=7/2 vanadium NMR line is masked by a large magnetic broadening which reflects the width of the field distribution at the vanadium site. On lowering T, the NMR line broadens drastically around 1.5 K and then saturates below 0.6 K. At a lower 12.548 MHz irradiating frequency, we checked that this saturation is field independent, and therefore reflects, as expected, a frozen field distribution in the GS. Upon closer inspection of the T-dependence of the lineshape, we note first the appearance of a broad background feature below 1.5 K. In order to track qualitatively this broad component we chose rather arbitrarily to plot the half width at 1/5 of the maximum in Fig. 3. Then the main central line, which width is roughly the width at half maximum of the spectra (open symbols in Fig. 3), starts to broaden rapidly and below 1 K, its lineshape changes from lorentzian-like to gaussian-like. The two distinct features, broad background and central line, in the low-T spectra suggest that the NMR line, below 1.5 K, is no more homogenous but results from at least two different types of magnetic environments of vanadium. This is probably related, as well, to the progressive freezing observed in macroscopic susceptibility. It is an important finding of this study as it demands a special magnetic ordering in the GS leading to two different V sites.

We now focus on the T=0.35 K spectra (Fig. 4) in the well established GS of volborthite. By comparison of the integrated intensity with $T > 2 \text{ K}$ data, we checked that all sites are detected at this low-T and we therefore probe the bulk properties of the sample. The top and bottom spectra have been obtained in the same condi-
tions except for a different duration $\tau$ in the pulse sequence $\pi/2 - \tau - \pi/2$. This contrast procedure allows us to separate the two components of the spectrum. They indeed prove to have different spin-spin relaxation times $T_2$ which we determined by standard $T_2$ measurements at $H = 1.845$ T and $H = 1.955$ T.

In the long time spectrum (top panel), the slowly relaxing ($T_2 = 105 \mu$s) broad background clearly stands out, without the fast relaxing ($T_2 = 60 \mu$s) gaussian-like component and appears to be rectangular shaped. An unshifted narrower line also appears on this spectrum. However, because of its much longer $T_2 = 240 \mu$s, it eventually represents less than 1% of the total sample and probably arises from some small impurity phase. The rectangular lineshape is a clear signature of the presence of one well defined frozen field $H_f$ at the vanadium site arising from the neighboring copper moments. The resonance condition writes $H_0 = 2\pi \nu_0/\gamma = \|H + H_f\|$ where $H$ is the applied field. Due to powder distribution, $H_f$ is randomly oriented with respect to $H$. In the limit $H_f \ll H_0$ one would expect a rectangular lineshape with cut-offs at $H_0 \pm H_f$. An exact derivation of the NMR line $P(H)$ yields

$$P(H) = (H_0^2 + H^2 - H_f^2)/(4H_fH^2)$$  

for $|H - H_0| < H_f$. The component labelled “ordered” in Fig. 4 is a fit with such a model with $H_f = 0.16$ T and a narrow distribution (0.02 T HWHM) of this frozen field. The solid line in the top panel is a gaussian fit to the NMR line, including the impurity phase. In order to produce a well-defined amplitude of the frozen field at the vanadium site, short-range order of the six neighboring Cu$^{2+}$ moments must exist. In a classical picture, the energy is minimized on the kagomé lattice, when the spins are at 120° from each other on each triangle. Following most of the theoretical works, we assume a $\sqrt{3} \times \sqrt{3}$ type short range order, sketched in the inset of Fig. 4 which corresponds to alternating chiralities (+ and - signs) on neighboring triangles. Such a short range order indeed leads to a well defined $H_f = 3H_{Cu}$ resulting field at the vanadium site, where $H_{Cu}$ is the frozen field arising from each Cu$^{2+}$. On the contrary, a uniform chirality order ($q = 0$) would lead to a null field at the vanadium site which cannot reproduce our NMR data. In addition, the classical $\sqrt{3} \times \sqrt{3}$ order favors local collective excitations made of a coherent out-of-plane rotation of the six spins belonging to a same hexagon as depicted in the inset of Fig. 4. It is remarkable that such excitations, which cost zero energy, do not affect the resulting field at the vanadium site, neither by hyperfine nor dipolar coupling, and are, therefore, ”filtered” out at the symmetric vanadium site. This could explain why we measured a small 1/T$_1$ which, besides, decreases at low temperature, as in usual static phases, whereas, in $\mu$SR experiments, muons which sit in less symmetric positions, still feel a strong dynamics which persists below $T_g$.

From $H_f$ and the hyperfine coupling constant, we get 0.14$\mu_B$ for the frozen Cu$^{2+}$ moment contributing to this slow relaxing component. This small value, compared to 1$\mu_B$ expected for a spin 1/2, demonstrates that zero point quantum fluctuations strongly affect the volborthite GS.

In the bottom panel, combining the formerly discussed slow relaxing components with a frozen gaussian-like
component ("disordered" label) results in the solid line which reproduces well the short time experimental spectra. Taking into account the different $T_2$ values, we evaluate the corresponding sample fractions, in the limit $\tau \to 0$, to be $\approx 80\%$ for the gaussian like component and $\approx 20\%$ for the rectangular-shaped one. A gaussian-like frozen component is easily obtained provided that the Cu$^{2+}$ frozen moments belonging to a same hexagon are randomly oriented as in the case of a spin glass. In this random picture, we extract also a small $0.44 \mu_B$ value for the frozen copper moment consistent with the previous estimate of the corresponding sample fractions, in the limit of several frozen field values, smaller than in the rectangular shaped case. A gaussian-like component could also come from the frozen copper moment consistent with the previous case and slightly distributed, arising from various other spin configurations. A crude illustration of this scenario can be obtained if one assumes a random distribution of the chiralities on the kagomé lattice. One finds that 4% of the hexagons are in the $\sqrt{3} \times \sqrt{3}$ configurations while the other configurations lead to either $H_{f} = 0$ (54%) or $H_{f} = \sqrt{3} H_{Cu}$ (41%). Our experimental value already indicates that, within this classical framework, the $\sqrt{3} \times \sqrt{3}$ configuration has to be favored by some mechanism. An exact quantum calculation of the possible states in a finite kagomé spin 1/2 cluster would certainly allow a better quantitative understanding of this gaussian-like component in this scenario. At the nanoscopic scale of the NMR probe, it is difficult to decide whether these two vanadium consistent with the previous scenario naturally explains the simultaneous occurrence of the glassy-like transition and the dynamical plateau in $\mu$SR experiments and is consistent with our finding of a two component NMR signal, arising from vanadium nuclei far and close to a defect.

In conclusion, volborthite which presents all the well established signatures of a spin liquid, namely no freezing at $T \approx \theta_{CW}$ and a dynamical plateau at $T \to 0$, allows, for the first time, a detailed NMR local investigation of the GS. This enabled us to study the internal field configurations and their dynamics. Further, this opens new avenues for refined theoretical calculations which are necessary to reveal the influence of the possible dissymmetry of the interactions and the actual texture of the GS.

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