Novel magnetic order in the kagome lattice of volborthite

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Abstract. The ground-state magnetic properties of the spin-1/2 quasi-kagome compound volborthite are discussed. Volborthite exhibits a peculiar phase transition to an unconventional ordered phase at 1 K. This phase is characterized by dense low-energy excitations and extremely slow spin fluctuations together with spin-wave like excitations, as evidenced by means of heat capacity and 51V NMR. To understand these features, we consider an exotic long-range order based on the 120º √3 × √3 spin structure, which allows local modes in the hexagons of the kagome lattice.

1. Introduction
The physics of the Heisenberg spins on the kagome lattice has been extensively studied for the last few decades [1]. Due to strong frustration, it is believed that there is an opportunity to discover an unprecedented ground state (GS) which lies between conventional long-range order (LRO) and a singlet-based state with a spin gap (Fig. 1). Possibly, the state is to be called a spin liquid [2]. A classical antiferromagnet with large spins may prefer the former GS with ordering temperature (TN) decreasing with increasing the empirical frustration factor f [3], -ΘCW/TN, where ΘCW is the Curie-Weiss temperature. By contrast, a quantum spin system tends to stabilize by forming spin singlet pairs and thus assumes a gapped state such as the resonating-valence-bond (RVB) state proposed by Fazekas and Anderson [4]. Recent exact diagonalization calculations on finite clusters found either a small (~J/20) or almost vanishing gap for the spin-1/2 Heisenberg kagome antiferromagnet (KAFM) [5, 6], which suggests that a long-range RVB (LR-RVB) state consisting of pairs of far-separated spins is possibly realized. Alternatively, a valence bond crystal (VBC) with a tiny gap may be stable [7]. In any regard, the GS of the KAFM certainly exists very close to the quantum critical point (QCP) between the two GSs, making it intriguing but difficult to study both theoretically and experimentally.

We have been focusing our attention on the material volborthite Cu₃V₂O₇(OH)₂·2H₂O which comprises Cu²⁺ ions carrying spin 1/2 on a distorted kagome lattice made of isosceles triangles (Fig. 2) [8]. The compound is considered to be a candidate for the spin-1/2 Heisenberg KAFM, though there is a distortion in magnetic couplings in the kagome lattice [9]. Moreover, there is a controversial issue on the nature of the magnetic couplings in volborthite: recent density-functional-theory calculations claim that the kagome lattice consists of frustrated J₁-J₃ chains together with third spins in between and thus can be far from the anisotropic kagome model [10]. The great advantage of volborthite over other compounds like herbertsmithite [11] and vesignieite [12] is that one can prepare high quality samples containing fewer impurity spins, i.e., only 0.07% of the total spin [13]. This allows one to investigate the intrinsic properties of the compound down to very low temperatures. High lattice coverage is
crucial to study compounds as expected to exist near a quantum critical point, because even a small perturbation by defects may influence the GS seriously; a glassy state is often induced, masking intrinsic properties [14].

**Figure 1.** Conceptual phase diagram for frustrated spin systems in two dimension such as the kagome antiferromagnet. Spin liquids may appear around a quantum critical point where long-range order (LRO) disappears as the empirical frustration factor \( f = -\Theta_{CW}/T_N \) becomes large with decreasing interlayer couplings or increasing quantum fluctuations, and the spin gap \( \Delta \) tends to vanish as the magnetic correlation length \( \xi \) becomes large. Otherwise, a certain exotic LRO containing topological excitations, a long-range resonating-valence-bond (LR-RVB) state or a valence bond crystal (VBC) could be stabilized as the ground state in this region.

The magnetic susceptibility, \( \chi \), of volborthite shows a broad peak at 20 K, with no anomaly down to 60 mK, indicating the absence of conventional LRO. Furthermore, it approaches a large, finite value at \( T = 0 \), providing evidence for a gapless GS. In contrast, \(^{51}\text{V}-\text{NMR}\) measurements reveal a magnetic transition at 1 K to a peculiar phase which is characterized by the presence of dense low energy excitations and unusually slow spin dynamics [13, 15]. These results strongly suggest that the GS of volborthite is neither a simple LRO nor a gapped state. Moreover, three magnetization steps are observed at magnetic fields of 4.3 T, 25.5 T and 46 T in measurements preformed up to 55 T [13]. The first step at 4.3 T is accompanied by a field-induced phase transition to a more magnetically ordered phase, as evidenced by \(^{51}\text{V}-\text{NMR}\) measurements [16]. Very recent magnetization measurements up to 68 T found a magnetization plateau at 0.39 of the saturation magnetization, which is significantly larger than the 1/3 as expected for a conventional up-up-down configuration on every triangular plaquette [17]. The magnetic field-temperature phase diagram determined by magnetization and \(^{51}\text{V}\) NMR is depicted in Fig. 2, which includes phases I, II, III, IV and V at low temperatures on increasing magnetic field.

In the present paper, we focus on the GS of volborthite as well as its response to weak magnetic fields below \( \mu_0 H_{c1} = 4.3 \) T. Particularly, the origin of the 1 K transition is investigated, trying to understand the nature of magnetic order in phase I. We find another transition or crossover at 2 T, above which the magnetic properties of phase I is significantly modified. We will propose a model based on the 120° spin structure with a \( \sqrt{3} \times \sqrt{3} \) unit to interpret these results.
2. Results

2.1. 1 K transition

The presence of a transition at low temperature in volborthite was first found by Bert et al. in their $^{51}$V NMR experiments [15]. They observed a broadening of the NMR spectrum below 2 K and a peak in the V nuclear spin relaxation rate ($1/T_1$). Unfortunately, however, the 1 K transition was not clearly detected, because the sample contained an amount of disorder that caused an additional broadening of the spectrum. Later, in an improved sample with less disorder, M. Yoshida et al. [16] found a sudden broadening below 1 K in the $^{51}$V NMR spectrum, as well as a sharp peak in $1/T_1$ that was nearly an order of magnitude larger than that reported by Bert et al. Since the transition becomes more pronounced as disorder is reduced, it must reflect an intrinsic property of volborthite. The transition temperature determined by the NMR experiments is insensitive to magnetic field below $H_{s1}$, as shown in the phase diagram of Fig. 2. In addition, the Lorentzian shaped NMR spectrum observed below 1 K indicates a spatially modulated spin structure such as a spin-density-wave (SDW) state or substantially short-ranged magnetic order [16]. On the other hand, $\mu$SR experiments by Fukata et al. found a slowing down of Cu spin fluctuations on cooling towards 1 K, followed by slow and nearly $T$-independent spin fluctuations persisting down to 50 mK [18].

The $1/T_1$ data at a magnetic field of 1 T obtained by M. Yoshida et al. is reproduced in Fig. 3 [16], showing a sharp peak at $T^* = 0.90$ K but no divergence, such as that observed in NiGa$_2$S$_4$ at 8.5 K [19]. Moreover, the $1/T_1$ is proportional to $T$ below 0.5 K, providing strong evidence for the presence of dense low energy excitations, as in a fermionic system like an ordinary metal. To our knowledge, no frustrated spin compounds have exhibited such $T$-linear behavior in $1/T_1$; the $1/T_1$ of NiGa$_2$S$_4$ is

**Figure 2.** Crystal structure and $H$-$T$ phase diagram of volborthite. A V atom located above or below each hexagon made of six Cu atoms, which is slightly shifted from the centre of the hexagon, probes the hyperfine field from the neighboring Cu spins. The phase diagram includes at least four phases I-IV separated by the three magnetization steps at $\mu_0 H_{s1} = 4.3$ T, $\mu_0 H_{s2} = 25.5$ T and $\mu_0 H_{s3} = 46$ T, followed by phase V showing a magnetization plateau above $\mu_0 H_p \sim 60$ T. There is another characteristic field at $\mu_0 H_{s0} \sim 2$ T.
proportional to $T^3$ [19] and that of $\kappa$-(ET)$_2$Cu$_2$(CN)$_3$ follows a power-law decay of $T^{1.5}$ at low temperatures [20].

Heat capacity measured by Nakazawa et al. is plotted in Fig. 3 [21]. Magnetic heat capacity, $C_m$, data obtained at magnetic fields of 0 and 1 T overlap to each other completely and show a kink at 1.05 K. Thus, there is a weak but well-defined thermodynamic phase transition that is not of second order but of higher order: we call this temperature $T_k$. Note that $T_k$ is higher by 0.15 K than $T^*$ for the $1/T_1$ peak, suggesting that slowing down of spins is not induced at the phase transition, but develops at lower temperatures after a narrow fluctuating crossover regime extending below $T_k$. This reminds us of a similar observation for the triangular Heisenberg antiferromagnet NaCrO$_2$, where the peak in $1/T_1$ is located at ~25 K well below $T_N = 40$-50 K, as determined by means of magnetization and heat capacity [22]. The importance of these observations has been pointed out and interpreted based on $Z_2$-vortex order by H. Kawamura [23].

The temperature dependence of the heat capacity provides important information about the GS and the nature of the transition [21]. $C_m/T$ is proportional to $T$ with a finite intersect toward $T = 0$ both above and below $T_k$. This implies that $C_m$ unusually has two contributions: $C_m = \gamma T + \beta T^2$. Note that phonon contributions have already been subtracted from raw data and only magnetic contributions are included in this insulating compound. Below $T_k$ the slope in $C_m/T$ increases suddenly and the intersect is much reduced. Since the data is limited above 0.8 K, it is difficult to obtain a reliable value for the low-temperature intersect. Assuming the same $T$ dependence as above $T_k$ yields $\gamma = 15$ mJ K$^{-2}$ mol-Cu$^{-1}$, which is less than half of the extrapolated value of 40.1 mJ K$^{-2}$ mol-Cu$^{-1}$ for the high-temperature state [21]. Further heat capacity measurements down to lower temperatures are in progress to attain a reliable value. In any regard, it is clear that finite $\gamma$ remains at low temperatures, which is consistent with the finite $1/T_1 T$ obtained from V NMR experiments. Thus, the most pronounced difference between the high- and low-temperature states concerns the form of the ‘density-of-states’.

**Figure 3.** (a) Magnetic heat capacity [19] and the relaxation rate, $1/T_1$, from $^{51}$V NMR experiments [16] and (b) schematic representations for the dispersion relations expected from their temperature dependences.

The second term in the heat capacity, proportional to $T^3$, is typically observed for spin-wave excitations in two-dimensional antiferromagnets. It is rather surprising to find such a conventional term in the unconventional GS of volborthite. It is to be noted, however, that many frustrated spin compounds have exhibited similar $T^3$ behavior even in the absence of conventional LRO [1, 3]. For example, it is well known that the spin-3/2 pyrochlore-slab (or kagome) compound SrCr$_{9}$Ga$_{12}$Sb$_{9}$O$_{19}$ (SCGO) shows a clear $T^3$ heat capacity below 4 K in the spin-glass state [24]; this is also the case for deuteronium jarosite [25] and NiGa$_3$S$_4$, both without LRO [26]. Therefore, common physics must exist
behind in these frustrated spin systems. In addition, the $T$-linear term has never been observed in other compounds except for a triangular lattice molecular compound $\kappa$-(ET)$_2$Cu$_2$(CN)$_3$ [27].

In order to explain these two terms in heat capacity, it is necessary to assume two independent branches in the dispersion relation, as schematically depicted in Fig. 3(b). Generally, a term with the $n$-th power of $T$ in heat capacity implies the existence of a branch having energy proportional to the $d/n$-th power of momentum transfer $q$, where $d$ is the dimension of the system. Thus, the $T$-linear and $T^2$ terms correspond to branches with $\omega \approx q^3$ and $q$, respectively. The former gives dense low energy excitations and the latter spin-wave excitations. We must now construct a reasonable model that can explain this unusual coexistence of the two branches. Furthermore, this model must give an explanation as to why $\gamma$ decreases and $\beta$ increases on cooling below $T_L$.

2.2. Anomaly in magnetization at 2 T

There is a weak anomaly in magnetization at a magnetic field of 2 T before the first magnetization step sets in [13]. Figure 4 shows an $M$-$H$ curve measured at the very low temperature of 60 mK, which first increases linearly, deviates upward slightly at around 2 T, and further rises up at 4.3 T. A tiny initial rise observed near $H = 0$ comes from about 0.1 % of almost free impurity spins. It is therefore not intrinsic. The deviation from the initial linear relation at 2 T is clearly detected in the derivative curve shown in the top of Fig. 4. This deviation is not due to the ‘tail’ of the first magnetization step, as the step begins at 3.7 T, where a kink exists in the derivative curve. The 2 T anomaly exists even at a relatively high temperature of 1.62 K, when the magnetization step has already disappeared.

![Figure 4. Magnetization versus magnetic field curve measured at 60 mK [13]. A derivative curve is shown in the top. Magnetizations measured at 0.06, 0.86 and 1.62 K after subtraction of an initial linear component and multiplication by a factor of 10 are also shown.](image)

We also measured magnetization at higher temperatures (Fig. 5); the 2 T anomaly is clearly observed at 2 and 5 K, and even at 10 K, and then tends to vanish on further heating. On the other hand, $M$-$T$ curves measured at $H = 1$ and 2 T overlap almost completely in the whole $T$ range below 30 K, as shown in Fig. 5(b), while deviations are observed above 3 T, particularly at $T < 10$ K, which is consistent with the behavior observed in the $M$-$H$ curves. Possibly, this deviation starts to grow below $T_p = 20$ K at a broad peak in magnetic susceptibility, indicating that it is not related to the 1 K transition but the development of magnetic correlations below $T_p$. Hence, the 2 T anomaly is essentially different from the magnetization steps at higher fields. The critical field $H_o$ is plotted in the $H$-$T$ phase diagram of Fig. 2.
One may notice that this 2 T anomaly resembles what is observed at a spin flop transition that often occurs in LRO Heisenberg spin systems with weak anisotropy. However, this should not be the case, because the anomaly exists at high temperatures even in the paramagnetic state. Alternatively, the $M-H$ and $M-T$ curves of Figs. 4 and 5 are reminiscent of similar behavior observed in spin-gapped compounds such as TlCuCl$_3$, where a field-induced magnetic transition occurs at $H_g = \Delta/(\mu_B)$ when

**Figure 5.** (a) $M-H$ curves measured at 2, 5, 10, 15, 20 and 25 K in a SQUID magnetometer upon increasing $H$. Corresponding data after subtraction of initial linear components are also plotted. (b) Temperature dependence of magnetic susceptibility measured at 1, 2, 3, 3.5, 4, 4.5 and 5 T on heating and cooling.

**Figure 6.** (a) Magnetic heat capacity measured by Yamashita et al. in magnetic fields of 0, 1, 3, 5 and 7 T [19] and (b) $^{31}$V NMR relaxation rate, $1/T_1$, measured by M. Yoshida et al. in magnetic fields of 1, 2, 4, 4.5, 5 and 6 T [16].

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the gap collapses. This has been interpreted as a Bose-Einstein condensation of magnons [28]. We will discuss on this issue later.

It is important to investigate how this 2 T anomaly affects heat capacity and NMR 1/T. Figure 6 shows their H dependences [16, 21]. Cw/T remains the same at 0 and 1 T, but shifts downward at low temperatures on further increasing H, with the 1 K kink being obscured. Note that γ for the low-temperature phase decreases gradually, if one assumes the T-linear dependence, and seems to vanish at 5 or 7 T, close to the boundary between phases I and II, while the slope β remains almost constant. The 1/T1 curve measured at 2 T shows a large (even larger than that at 1 T) peak at around 0.9 K and exactly follows the 1 T curve at low temperatures with the same magnitude of 1/T1. The 0.9 K peak survives at 4 and 4.5 T, though it becomes small, and the T-linear terms at low temperature remain. At 5 or 6 T, in contrast, the peak shifts to a higher temperature (~1.3 K), which corresponds to the transition to phase II on cooling, and the T-linear term disappears; the 6 T data below 1 K is proportional to T−5 [16]. Therefore, the magnetic state at zero field appears robust below a critical field of approximately 2 T, while the density of the low energy excitations are gradually reduced with increasing H above 2 T and may completely disappear at Hc1.

3. Discussion

Here we discuss the magnetic state of volborthite in phase I, at low magnetic field. Summarizing the related observations obtained so far: (1) magnetic susceptibility decreases rather steeply below Tc ∼ 20 K, (2) a high-order magnetic phase transition sets in at Tc = 1.05 K, (3) NMR 1/T exhibits a peak at a slightly lower temperature of T′ = 0.90 K, (4) the Lorentzian shape of V NMR spectrum observed below T′ suggests a SDW-like order, (5) two kinds of excitations exist both above and below Tc; dense low energy excitations characterized by T-linear contributions in heat capacity as well as in 1/T1, and 2D spin-wave like excitations, (6) γ decreases and β increases below Tc, and (7) a change in the magnetic state occurs at μ0Hc0 ∼ 2 T, above which the density of the low energy excitations starts to decrease before vanishing at Hc1. In order to explain these features, we will consider a simple model based on the $\sqrt{3} \times \sqrt{3}$-type LRO of spins.

3.1. Gap or LRO

One theoretical prediction for the spin-1/2 KAFM is a LR-RVB state with a tiny singlet-triplet gap filled by a singlet continuum [5]. Thus, one would not expect gapped behavior in the heat capacity but only in the magnetic susceptibility. Since the magnitude of a spin gap is inversely proportional to the magnetic correlation length, $\xi$, or the separation of paired spins, the LR-RVB state contains both far-separated singlet pairs as well as near-neighbor ones, as depicted in Fig. 1. On the other hand, once LRO sets in due to some perturbations (defects, anisotropies, etc.), the 120º spin structures of the $\sqrt{3} \times \sqrt{3}$ type would be selected by the order-by-disorder mechanism [1]. In the $\sqrt{3} \times \sqrt{3}$-type coplanar LRO, three sublattice spins on every triangular plaquette form a 120º angle and are arranged on the kagome lattice as depicted in Fig. 1 and Fig. 7(a). It is, in other words, a staggered order of the scalar chirality associated with each triangular plaquette. However, this state always remains imperfect even at T = 0, because a local zero-energy mode on every hexagon, called the weathervane (W) mode, can destroy the order by introducing chirality domains [1, 29, 30]. The W mode is composed of a coherent out-of-plane rotation of six spins belonging to one hexagon (Fig. 7(b)) and costs no energy, if only nearest-neighbor antiferromagnetic couplings are considered. The $\sqrt{3} \times \sqrt{3}$ structure may be less stable for spin 1/2 than in the classical limit owing to quantum fluctuations [31].

Apparently, there is no spin gap in volborthite. However, the magnetic susceptibility decreases below Tc towards a 20%-reduced value at T = 0. This reduction is small for a gapped system but larger than expected for SRO in 2D. Thus, it is plausible to assume that certain singlet correlations develop below Tc. In fact, diffuse neutron scattering experiments find nearest-neighbor antiferromagnetic or singlet correlations at 15 and 5 K [32].

On this issue, it is illustrative to consult previous results on spin ladder compounds such as SrCu2O3 [33] and LaCuO2.5 [34]. The former has a well-defined singlet GS with a large gap of $\Delta \sim 420$
K, while the latter falls into LRO at 125 K [35, 36]. Nevertheless, the χ of LaCuO$_{2.5}$ exhibits very similar gapped behavior with $\Delta \sim 470$ K as SrCuO$_2$. This is because LaCuO$_{2.5}$, having a larger interladder coupling, exists close to the QCP in the LRO side. Quantum Monte Carlo simulations by M. Troyer et al. found a decoupled ladder regime at intermediate temperatures that shows pseudogap-type behavior similar to uncoupled ladders [37]. In such a case, singlet correlations develop below $T \sim \Delta/k_B$, but LRO of reduced spins is finally reached on further cooling.

By analogy, the χ of volborthite must represent a development of singlet correlations corresponding to a pseudogap of the order of $J/2$. If so, the 2 T anomaly might correspond to the collapse of the lowest bounds of the pseudogap, that is $2T \sim 1.5$ K $\sim J/50$. Recent ESR experiments by H. Ohta et al. seems to be in line with this scenario: they found a variation of the $g$ factor below $T_p$, suggesting the development of a large spin gap, and also a small gap excitation of 40 GHz $\sim 1.9$ K at a low temperature of 1.8 K [38]. Resemblance to spin-gapped compounds such as TlCuCl$_3$ in the $M-H$ and $M-T$ curves, as mentioned before, supports this speculation. Hence, the GS of volborthite could have been a LR-RVB state or other spin liquid states that have a density-of-states in an approximate range between $J/50$ and $J/2$, if LRO was not reached down to $T = 0$.

Figure 7. (a) Ideal $\sqrt{3} \times \sqrt{3}$ spin structure. The three sublattices, indicated by blue, green and yellow arrows on the lattice points, form 120° angles with respect to each other. ‘+’ or ‘-’ on each triangle represents the sign of the scalar chirality. A large arrow inside a hexagon shows the magnitude and direction of the internal magnetic field $H_{int}$ from the surrounding six Cu spins at a V nucleus located nearly above or below the center of the hexagon (Fig. 2). (b) Snapshot of a spin arrangement after a weathervane mode within the central hexagon. When six spins on the centre hexagon are collectively rotated by 120°, as a result of the 180° out-of-plane precession around the axis of the outer spins on the kagome star, a chirality domain is generated, as shown by the broken circle, and the $H_{int}$ at the V sites in the surrounding hexagons is reduced by $1/\sqrt{3}$.

3.2. Magnetic ground state of volborthite

Very recent neutron scattering experiments on volborthite by Nilsen et al. found semi-classical SRO developing below 5 K and accompanying spin-wave like excitations [32]. Although the spin configuration at the lowest temperature was not determined, the observed SRO seems partly compatible with the $\sqrt{3} \times \sqrt{3}$ structure with a short magnetic correlation length. On the other hand, Bert et al. observed a Gaussian like frozen component in their $^{51}$V NMR experiments, accounting for 80%
of $^{51}$V nuclei [15], which is distinguished from an ordinary powder pattern for LRO. This was attributed to the formation of a $\sqrt{3} \times \sqrt{3}$ structure with disordered chirality.

The $^{51}$V nucleus is located above or below the center of each hexagon (not exactly the center as shown in Fig. 2) and experiences an internal magnetic field $H_{\text{int}}$ from neighboring six Cu spins. As illustrated in Fig. 7(b), once each spin on the hexagon at the center of the figure is rotated by 120º due to the W mode (180º precession about the axis of the outer spins in star, but only 120º rotation), thus generating a chirality domain, the V nuclei in the neighboring six hexagons should feel a reduced $(1/\sqrt{3}) H_{\text{int}}$ from surrounding Cu spins [15]. This is because all three sublattice spins now coexist on each of these hexagons. Note that the internal field at the V nucleus in the center hexagon remains the same as before: the hexagon only contains two spin orientations. Assuming a random distribution of chirality frozen through this process may result in such a Gaussian like spectrum. Thus, the NMR results may be consistent with classical SRO based on the $\sqrt{3} \times \sqrt{3}$ structure [15]. On one hand, they seem to be inconsistent with implications from the previous $\mu$SR experiments, which found slow and nearly $T$-independent spin fluctuations at low temperatures from 1 K to 50 mK [18]. This contradiction may be due to the fact that the muon is possibly not in a symmetric position in the lattice and feels different spin fluctuations from neighboring Cu spins.

![Figure 8](image)

Figure 8. Schematic representation of possible arrangement of weathervane (W) modes or hexagon doublets (HDs). The three flavours of spin in the original $\sqrt{3} \times \sqrt{3}$ structure are represented by dots with different colors. A thick circle on a hexagon represents a W mode or a HD. A $2a \times 2a$ arrangement of HDs is depicted near the centre of the figure, and a $\sqrt{3} a \times \sqrt{3} a$ one in the lower right. Spins belonging to the HDs can fluctuate, while other spins surrounding the hexagons to complete the kagome stars are completely fixed in their directions and so perfectly long-range ordered. It is assumed in the snapshot of the $2a \times 2a$ arrangement that the dots in the hexagons marked by A, B and C have rotated by 60º from their original positions, which reduces the $H_{\text{int}}$ of the surrounding hexagons to ‘$m$’ or ‘0’. ‘I’, ‘$m$’ and ‘0’ inside some hexagons mean large, medium and zero internal magnetic fields at the V site, respectively. Depending on the mutual spin arrangements, the $H_{\text{int}}$ can vary over time and be distributed.

The Lorentzian-like NMR spectrum observed below 1 K by M. Yoshida et al. must then have the same origin [16]. It is likely that the W modes are moving around quickly in the developing SRO at high temperatures, so that the NMR signal remains sharp without static $H_{\text{int}}$ at the V site within the NMR timescale. Below $T_k = 1.05$ K, as LRO sets in, their movement slows down and may freeze to
generate static but distributed internal magnetic fields, as in an SDW state. However, it is more likely from the viewpoint of entropy that the W modes are regularly arrayed in the kagome net at \( T = 0 \).

Let’s consider one possible arrangement of W modes, as illustrated in Fig. 8, in which they form a triangular lattice with a \( 2a \times 2a \) unit. This is the pattern which results in maximum density, assuming no overlap between kagome stars (hexagon plus surrounding six lattice points). Another possible arrangement with higher density by one-third has a \( \sqrt{3}a \times \sqrt{3}a \) unit, which is attained by relaxing the previous condition, but allowing no overlap between hexagons. Considering unusual characteristics for the former pattern, \( H_{\text{int}} \) on the V nucleus in every W mode is always the same as in the perfect LRO, irrespective of the rotation or the exchange of spins on the hexagon, while that in the intervening hexagons can vary among 1, \( 1/\sqrt{3} \), and 0, depending on the configurations in the neighboring two W modes. Taking this into account, one would expect a continuous distribution in \( H_{\text{int}} \) giving a Gaussian or Lorentzian like \(^{51}\text{V} \) NMR spectrum even. Note that, still in the ordered arrangement of W modes, there remains a degree of freedom inside each W mode. We believe that this sort of coexistence of order and disorder or fluctuations such as shown in Fig. 8 represents one interesting aspect of the kagome physics.

3.3. Magnetic excitations

The origin of the dense low-energy excitations observed in \( C_\alpha \) and \(^{51}\text{V} \) NMR can be the W mode, though such a classical mode may not survive down to low temperatures in the presence of anisotropies, instead, freezing with a gap. It would be interesting if there is a quantum analogue for the W mode. We will consider two distinct spin arrangements for one hexagon or one kagome star, which appear in the course of the out-of-plane rotation when the spin plane of the kagome star coincides with that of the rest, to be totally coplanar. This is the case depicted in Fig. 7. This means that there are two degrees of freedom per hexagon carrying entropy \( k_B \ln 2 \), which results in huge entropy of \( 1/3 \) of \( \gamma \text{ln} 2 \) (1.92 J K\(^{-1}\)) in total. Let’s call this degree of freedom a hexagon doublet (HD).

We think that the observed \( T \)-linear behavior in heat capacity and \( 1/T \) comes from flipping between the two configurations of this hexagon doublet. Assuming that the total entropy of \( (1/3)\gamma \text{ln} 2 \) is spread over a wide temperature range such as \( k_B T \) or \( T_{\text{p}} \), one would expect \( \gamma = 25 \) or 96 mJ K\(^{-2}\) mol-Cu\(^{-1}\), reasonably close to 40 mJ K\(^{-2}\) mol-Cu\(^{-1}\) as observed above \( T_k \). The reduction of \( \gamma \) below \( T_k \) suggests that the number of HDs has decreased through the LRO of spins or by the order of HDs.

It is important, moreover, to notice that spins outside HDs are fixed in their directions and perfectly ordered in the long-range way, which should give spin-wave excitations, as in fact detected in heat capacity as well as in the neutron scattering experiments [32]. The \( T^2 \) term also exists above \( T_k \) with a smaller coefficient, indicating that the spin lattice is harder at high temperatures. The presence of spin-wave like excitations above \( T_k \) may be related to “disguised” spin waves theoretically predicted in the coplanar or nematic state for the classical Heisenberg KAFM [39, 40]; possibly, spin-wave excitations may exist both above and below \( T_k \) with the stiffness changing across \( T_s \), as a result of the LRO. Since the \( T^2 \) heat capacity has also been observed in other kagome and triangular compounds, similar spin-wave like excitations must be commonly involved in 2D frustrated spin systems existing near a QCP.

Concerning the presence of a pseudogap as a trace or a fingerprint of a LR-RVB state, states filling up the gap are obviously magnetic, not nonmagnetic as expected from theory, and can be associated with true or “disguised” spin waves and also with the degree of freedom from the HD. The observed reduction in \( \gamma \) above 2 T may indicate that the density of the low energy excitations is reduced by the contamination of triplet states pulled down by the magnetic field.

3.4. Implications for states in magnetic fields

What is happening under higher magnetic fields, particularly at the three magnetization steps, remains mysterious and may be investigated in line with the present model. The W mode should play a role as far as the three-sublattice spins in the \( \sqrt{3} \times \sqrt{3} \) spin structure remain equivalent. On the other hand, above the second magnetization step where magnetization is largely increased, a ferrimagnetic state must be responsible with two sublattice spins (e.g. green and yellow spins in Fig. 7) form a smaller
angle than 120º, as predicted for a distorted kagome system [41]. There is another mystery concerning volborthite as well as vesignieite, that is, a large enhancement in magnetization from 1/3 at the magnetization plateau [17]. Finally, we would like to point out that a similar hexagon-based phenomenon has been theoretically predicted for the quantum KAFM at a high magnetic field corresponding to $3J$: a jump in magnetization takes place from 7/9 to 1 (fully polarized state), when the density of local magnons on the hexagon reaches a maximum at a $\sqrt{3} \times \sqrt{3}$ unit [42].

4. Concluding remarks

In summary, the magnetic ground state of the spin-1/2 quasi-kagome antiferromagnet volborthite has been investigated, and an exotic long-range order based on the $\sqrt{3} \times \sqrt{3}$ spin structure has been proposed. Irrespective of the details of the ordering, it is apparent that volborthite lies in the left side of the phase diagram in Fig. 1, which seems to contradict all theoretical models thus far considered for spin-1/2 Heisenberg KAFM. The reason for this is not clear at the moment, but may be related to the distortion of the kagome lattice or deviations from the ideal nearest-neighbor kagome model. However, we would like to point out that our discussion here has assumed only the presence of a local $\sqrt{3} \times \sqrt{3}$ spin structure, independent of microscopic magnetic couplings, and thus should not be specific to volborthite.

One interesting issue of frustration physics is to find an optimal route to lift macroscopic degeneracy arising from geometrical frustration. Even though quantum fluctuations are strong enough to render a ‘liquid’ state viable for the spin-1/2 KAFM, it seems difficult to attain such a liquid state in real compounds. It is well known now that local excitations appear in some spinel compounds having the pyrochlore lattice [43, 44], which may be introduced to avoid frustration and stabilize LRO. Provided that the incorporation of local modes such as the weathervane mode to the kagome lattice is realistic, we think that such an exotic LRO as mentioned here could be an alternative to spin liquids in the presence of some perturbations. The introduction of certain local collective modes into LRO of spins might be a general scheme for highly frustrated spin systems to reach non-degenerate GSs. Nevertheless, it is to be noted that there must be a fingerprint for the unrealized, true GS at elevated temperatures above $T_N$ or at excited states, allowing us to study its nature experimentally. Since there still remains uncertainty and considerable mystery about the GS of the spin-1/2 KAFM, further systematic study on various kagome compounds as well as theoretical models is required.

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