Magnetization Step in Spatially Distorted Heisenberg Kagomé Antiferromagnets

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Motivated by a recent experiment on volborthite, a typical spin-1/2 antiferromagnet with a kagomé lattice structure, we study the magnetization process of a classical Heisenberg model on a spatially distorted kagomé lattice using the Monte Carlo (MC) method. We find a distortion-induced magnetization step at low temperatures and low magnetic fields. The magnitude of this step is given by \( \Delta m_x = |1 - \alpha|/3\alpha \) at zero temperature, where \( \alpha \) denotes the spatial anisotropy in exchange constants. The magnetization step signals a first-order transition at low temperatures, between two phases distinguished by distinct and well-developed short-range spin correlations, one characterized by spin alignment of a local 120° structure with a \( \sqrt{3} \times \sqrt{3} \) period, and the other by a partially spin-flopped structure. We point out the relevance of our results to the unconventional steps observed in volborthite.

KEYWORDS: volborthite, magnetization step, geometrical frustration, kagomé lattice, Heisenberg model

In antiferromagnets on the kagomé lattice, geometrical frustration effects are believed to suppress the conventional magnetic long-range order and induce a large degeneracy of the ground state. It opens a possibility of realizing spin-liquid states, which are spin analogues of liquids.\(^1\) Volborthite Cu\(_4\)V\(_2\)O\(_7\)(OH)\(_2\)·2H\(_2\)O is known as a nearly ideal spin-1/2 kagomé antiferromagnet.\(^2\) Measurements of the magnetization and specific heat for this compound indicate the absence of the conventional magnetic long-range order down to 50 mK.\(^3,4\) Therefore, it is proposed that this material offers evidence of the quantum spin-liquid state in nature.\(^4\)

Recent studies on volborthite have revealed the existence of three unconventional steps in the magnetization curve.\(^3,5\) These steps are not anticipated in the magnetization process of the isotropic kagomé Heisenberg model in the literature\(^5,6\) and their origin is not yet understood. A MC study of the classical Heisenberg model has clarified the existence of the magnetization plateau at one-third of the saturation magnetization \( (m_{sat}/3) \) at finite temperatures, interpreted as the order-by-disorder effect.\(^5\) Even for the quantum Heisenberg model \( (S = 1/2 \text{ and } 1) \), an exact diagonalization study has shown a similar magnetization plateau at zero temperature.\(^6\) However, the magnetization step has not been found in the isotropic kagomé Heisenberg model.

In this Letter, to shed light on the origin of the unconventional steps observed in volborthite, we calculate the magnetization curve in the antiferromagnetic classical Heisenberg model on the spatially distorted kagomé lattice by using the MC method. In our viewpoint, structural distortion, which inevitably exists in volborthite,\(^4\) holds the key to understanding the magnetization step. This structural distortion induces a spatial anisotropy in exchange interactions. Therefore, as a simple model, we employ an anisotropic \((J_1-J_2)\) kagomé Heisenberg model to describe the magnetization process observed in volborthite. We find distortion-induced first-order phase transitions at low temperatures and low magnetic fields. In the vicinity of this first-order phase transition, step-like behaviors of the magnetization curve are found and spin structure factors change drastically from local 120° structures to spin-flopped structures. We also determine the \( h-T \) phase diagram for the spatially anisotropic kagomé Heisenberg model.

\[ H = J_1 \sum_{\langle i,j \rangle_1} S_i \cdot S_j + J_2 \sum_{\langle i,j \rangle_2} S_i \cdot S_j - h \sum_i S_i^z, \]

where \( S_i \) denotes the Heisenberg classical spin, \( h \) denotes the external magnetic field, and \( \langle i,j \rangle_1 \) and \( \langle i,j \rangle_2 \) denote nearest-neighbor sites on AB/AC chains and BC chains, respectively. In the kagomé lattice, the unit cell contains three sites A, B, and C, as shown in Fig. 1. The spatial anisotropy induces different antiferromagnetic couplings on each triangle: two \( J_1 \) bonds and one \( J_2 \) bond. For simplicity, we set \( J_1 = 1 \) and \( J_2 = \alpha J_1 \). We simplify the

Fig. 1. (Color online) An \( L \times L \) \((L = 2a)\) distorted kagomé lattice. Lattice sites labeled A, B, and C constitute a unit cell (dashed line triangle). The number of spins is \( N = 3L^2 \). Bonds along two directions have the exchange constant \( J_1 \) (thin blue lines), while the bond along the third direction has the exchange constant \( J_2 = \alpha J_1 \) (thick red lines). For volborthite, it is plausible that \( \alpha > 1 \).

Our model Hamiltonian is defined in the form
Hamiltonian as
\[ H = \sum_{\text{triangles}} \left[ (S_A \cdot S_B + \alpha S_B \cdot S_C + S_C \cdot S_A) - \frac{h}{2} (S_A^2 + S_B^2 + S_C^2) \right]. \tag{2} \]

The summations are taken over upward and downward triangles. The lattice has no distortion when \( \alpha = 1 \). There are two simple limits for this model. For \( \alpha \to 0 \), the lattice becomes a decorated square lattice, with additional sites at the midpoints of square lattice edges. In this limit, the ground state is ferrimagnetic. For \( \alpha \to \infty \), the lattice becomes isolated antiferromagnetic chains and free spins, and is equivalent to the one-dimensional lattice. In volborthite, we infer that \( \alpha \) is larger than unity from a comparison of bond lengths. The magnitude of the anisotropy is estimated to be less than 20% from theoretical analysis.\(^7\) We consider both kinds of anisotropy, especially \( \alpha = 1.05 \) and \( \alpha = 0.95 \), but perform detailed analyses of the \( \alpha = 1.05 \) case.

We clarify thermodynamic properties of this model by using MC simulations. The Metropolis algorithm is employed. We start the simulations from random initial states. Spins are updated in the sequential order on the lattice. We also perform one over-relaxation update per MC step to accelerate efficient sampling.\(^8\) At every temperature and field, \( 5 \times 10^4 \) MC steps are taken for equilibration. These are followed by measurements conducted for more than \( 5 \times 10^5 \) MC steps. Finally, the results are averaged over more than 8 independent runs to estimate statistical errors. At low temperatures \( T \leq 0.01 \), we use the exchange MC algorithm.\(^9\) Simulations are conducted for system sizes up to \( L = 72 \) \((N = 15552)\) under the periodic boundary conditions. We set the Boltzmann constant \( k_B = 1 \).

In Fig. 2(a), we show the magnetization \( m_z \) parallel to applied fields at several choices of temperatures as a function of magnetic fields. For both \( \alpha > 1 \) and \( \alpha < 1 \), we have observed a magnetization plateau \( m_{\text{sat}}/3 \) at low temperatures, which has already been reported by Zhitomirsky for the isotropic \((\alpha = 1)\) kagomé lattice.\(^5\) Owing to the distortion, the magnetization plateau becomes much wider. This tendency is consistent with the results of the exact diagonalization for a spin-1/2 distorted kagomé Heisenberg model.\(^5\)

As shown in Fig. 2(b), we have observed step-like behaviors at low temperatures and low magnetic fields. To determine whether these step-like behaviors are the first-order phase transitions in the thermodynamic limit, we calculate the energy distribution \( P(E) \) up to \( L = 84 \). If the transition is of the first order, the energy distribution \( P(E) \) should be bimodal at the transition temperature. As shown in Fig. 2(c), we find a clear two-peak structure around the transition point. This result shows evidence for the first-order phase transitions at low temperatures. These first-order phase transitions appear only when the lattice has anisotropies (\( \alpha \neq 1 \)). The transition field increases monotonically with increasing temperature. The first-order jump becomes reduced with increasing temperature and vanishes at a finite-temperature critical point, as we detail below.

The origin of the first-order phase transitions is well understood by considering the zero temperature limit. To analyze the ground-state properties, we rewrite the Hamiltonian as
\[ H = \sum_{\text{triangles}} \left[ \frac{\alpha}{2} \left( S_{\Delta} - \frac{h}{2\alpha} e_z \right)^2 + \frac{1 - \alpha}{2\alpha} h S_A^z + \text{const.} \right], \tag{3} \]
where \( S_{\Delta} = S_A + S_B + S_C \). For \( h = 0 \), the energy is minimized with \( S_{\Delta} = 0 \). The ground state, which satisfies the constraint \( S_{\Delta} = 0 \), has an infinite degeneracy and
the magnetization is zero. For $0 < h < \min(2, 4\alpha - 2)$, the energy is minimized with $S_x = (h/2\alpha)\epsilon_z$ and $S_{\gamma} = -\text{sign}(1 - \alpha)$, and hence $S_B^x = S_C^x = [h + 2\text{sign}(1 - \alpha)]/(4\alpha)$. Therefore, at zero temperature, we obtain the magnetization as
\begin{equation}
m_z = \frac{S_A^x + S_B^x + S_C^x}{3} = \frac{h + 2|1 - \alpha|}{6\alpha}.
\end{equation}
Equation (4) indicates that the magnetization jumps by an infinitesimal magnetic field at $T = 0$. Although thermal fluctuations reduce the magnitude of this jump and shift the transition point to higher fields, this first-order phase transition still survives at sufficiently low temperatures, as we have already shown by MC calculations.

From the above analyses, it turns out that the origin of the first-order phase transition is a level crossing of the ground state. When the spatial anisotropy exists, the macroscopic degeneracy of the kagomé antiferromagnet is partially lifted by an infinitesimal magnetic field, i.e., under magnetic fields, the ordered vector becomes $q = (0, q_y)$, where the range of $q_y$ is given by $-\pi \leq q_y \leq \pi$.

To identify the nature of the first-order transition, we calculate at $T > 0$ the spin structure factors defined as
\begin{equation}
S^{xy}(q) = \frac{1}{N^2} \sum_{i \neq j} \left( S_i^x S_j^y + S_i^y S_j^x \right) e^{i q \cdot (R_i - R_j)},
\end{equation}
where the index $l$ denotes the positions of the three sites on the unit cell, and $i, j$, and $R_{i,j}$ denote the coordinates of the $(i,j)$-th unit cell on the triangular Bravais lattice. We take the lattice period (a side length of the square in Fig. 1) as the length unit and hence the interspin distance equals 1/2. The first Brillouin zone is a square bounded by $-\pi \leq q_x, q_y \leq \pi$.

As shown in Fig. 3, the structure factors $S^{xy}(q)$ drastically change when we cross the first-order transition point. At lower fields [$h = 0.1, T = 0.01$, see Fig. 3 (b)], $S^{xy}(q)$ has broad peaks at $q = (\pm 2\pi/3, \pm 2\pi/3)$, which corresponds to a $\sqrt{3} \times \sqrt{3}$ structure in real space. At higher fields [$h = 0.2, T = 0.01$, see Fig. 3(c)], the structure factor has sharp peaks at $q = (0, \pm \pi)$, indicating the real space pattern shown in the lower panel of Fig. 3(c). In the magnetic structures in Fig. 3(c), spins on A sites align parallel to the magnetic field indicating a partial spin flip under magnetic fields. Along a BC chain, the $xy$ components of spins on the B sites are all parallel to each other and are antiparallel to all the spins on the C sites. Along an AB chain, the spins on the B sites align alternately. Although the ground states are degenerate among any ordered vector $q = (0, q_y)$, thermal fluctuations appear to favor the $q = (0, \pm \pi)$ configuration via the order by a disorder effect.

We obtain phase boundaries for $\alpha = 1.05$ at lower temperatures and lower fields $h < 2$, as shown in Fig. 4. From the location of the steps, we determine the first-order transition line. Because this first-order transition is characterized by the jump of the magnetization and does not involve any explicit symmetry breaking, its nature is inferred to be essentially the same as that of the gas-liquid type. Namely, the uniform magnetic susceptibility diverges at the critical end point of this first-order phase transition as the density fluctuation diverges at the critical end point of the gas-liquid transition. Thus, the first-order phase transition line terminates at the critical point, and a crossover line appears beyond the critical point. This crossover line is determined by the peak of the specific heat and the susceptibility. Since there is an exact correspondence between the gas-liquid transition and the two-dimensional Ising transition, the universality class of the critical point of this first-order transition belongs to that of the Ising model. Therefore, as one approaches the critical point along the crossover line, the susceptibility diverges as $x_{\text{peak}} \propto [T - T_c]^{-\gamma}$ or $|h - h_c|^{-\gamma}$, where $\gamma = 7/4$ for the Ising universality class.

Although continuous symmetry breaking is prohibited in two dimensions at $T \neq 0$, a quasi-long-range order may occur in the case of the XY anisotropy. Because the effective symmetry of the Heisenberg model becomes of the XY type under the magnetic fields, the quasi-long-range order of the spin itself or the tricatic order, i.e., Berezinskii-Kosterlitz-Thouless (BKT) transition, may occur. To examine the possibility of the

![Fig. 3.](image)

(Color online) (a) Magnetization curve around the first-order transition at $T = 0.01$. Statistical errors are smaller than the symbol size. (b) and (c) Spin structure factors for $\alpha = 1.05$, $L = 36$ (upper panel) and corresponding schematic spin configurations in real space (lower panel) around the first-order transition. In (b), $h$ is lower than the transition field $h_c \approx 0.16$ ($h = 0.1, T = 0.01$), where the structure factor shows a $\sqrt{3} \times \sqrt{3}$ pattern. In (c), $h$ is higher than $h_c$ ($h = 0.2, T = 0.01$), where the structure factor shows a $q = (0, \pm \pi)$ pattern. The peak values are $S(q) = 3.21(1) \times 10^{-4}$ in (b) and $S(q) = 2.6(2) \times 10^{-4}$ in (c) (the last digit in the parentheses indicates the error bar). In spin structure factors, we illustrate the regions $-\pi \leq q_x \leq \pi$ and $-\pi \leq q_y \leq \pi$ in the momentum space. In schematic spin configurations illustrated in the lower panels of (b) and (c), the unit cells of each pattern are shown by a dotted line.)
quasi-long-range order, we have calculated the spin correlation function and estimated the correlation lengths below the crossover line. It seems that the spin correlations along the AB and BC chains decay exponentially for a system size $L \geq 48$ even at the lowest accessible temperature. Therefore, we tentatively conclude that no BKT phase of spins exists under magnetic fields, although detailed studies are left for future studies. Although the possibility of the other BKT-type phase transitions is not excluded by our calculation, such transitions are unlikely because the system becomes an effectively disconnected one-dimensional BC chain at zero temperature (see Fig. 3) and has no two-dimensional long-range order. This absence of two dimensional long-range order indicates the fact that no BKT transition occurs at finite temperatures.

We now examine the relevance of our results to the unconventional steps observed in volborthite. In our model, we find one distortion-induced magnetization step. This first-order transition is similar to the step-like behaviors in volborthite, although three steps are observed in the experiment. To identify the relationship between the experiment and the result of our model, we estimate the upper bound of the magnetization at the transition point. At $T > 0$, the transition occurs between two nonzero $m_z$’s, namely $m^+$ and $m^-$, at a transition field $h_{1st} > 0$. As can be seen from Fig. 2(b), for all temperatures, $m^+$ is nearly the same as that of the zero-temperature magnetization, i.e., $m_z(h = h_{1st}) = (h_{1st} + 2(\alpha - 1))/(6\alpha)$. Since the distortion is 20% at most ($\alpha < 1.2$) and the transition occurs at $h_{1st} < h_c \sim 0.11$, we obtain $m^+ \lesssim 1/14$. By considering the experimental magnetization where the three steps occur ($m_{sat}/3, m_{sat}/6,$ and $m_{sat}/45$), if we assign $m_{sat}/14$ to an upper bound of one of them, it is likely that the $m_{sat}/45$ step corresponds to the present distortion-induced step. The sudden change in the spin structure factors from $q = (\pm 2\pi/3, \mp 2\pi/3)$ to $q = (0, \pm \pi)$ structures at the first-order transition may be detected in neutron scattering and nuclear magnetic resonance experiments.

In the experiment, the transition point does not sensitively depend on $T$, while our results imply that it should decrease to $h_{1st} = 0$ when $T \to 0$. This discrepancy may be due to quantum effects under which the $q = (\pm 2\pi/3, \mp 2\pi/3)$ structure may be stabilized even at $h \neq 0$ and $T = 0$. It is intriguing to identify the critical point for volborthite and to determine whether the first-order transition survives under quantum fluctuations.

In summary, by using the MC method, we have clarified the thermodynamic properties of the classical Heisenberg antiferromagnets on a distorted kagomé lattice under magnetic fields. The distortion-induced magnetization step appears at low temperatures and low magnetic fields. Estimating the upper bound of the step size, we conclude that this is the first-order transition induced by spatial anisotropy and corresponds to the step at the lowest field observed for volborthite. The spin structure factor shows a sharp change at the transition, which may be detected experimentally.

Clarifying the origins of the two other steps in the experiment remains for future studies. Other interactions in volborthite such as next-nearest neighbor interactions and Dzyaloshinskii-Moriya interactions may give rise to additional unconventional phase transitions. Moreover, our results are obtained for the classical model while volborthite consists of quantum spin-1/2 spins. It is an interesting future work to determine whether quantum fluctuations suppress the first-order transition observed in the classical system, leading to a crossover with a similarity to the experiment in which the temperature dependence of the transition field is weak.

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