Spin-1/2 kagome antiferromagnets (KAFMs) with strong quantum fluctuations are one of the most intriguing playgrounds in the field of highly frustrated magnetism. In spite of numerous theoretical and experimental studies in the last decade, the nature of the ground state of the spin-1/2 KAFM remains an open question. One of the most possible ground state proposed by exact diagonalization studies is a nonmagnetic spin-liquid state with a small spin gap estimated to be on the order of $J/20$, which is filled with a continuum of singlet excitations, where $J$ is the nearest-neighbor exchange coupling constant $[1]$. On the other hand, we need experiments on an actual material to realize the spin-1/2 KAFM. However, only a few model systems are known at present, where some extrinsic factors like three-dimensionality, disorder effects, and lattice distortion have prevented us from deducing the intrinsic properties of the KAFM at low temperatures.

Two $\text{Cu}^{2+}$ minerals, namely, herbertsmithite $\text{ZnCu}_3(\text{OH})_6\text{Cl}_2$ $[2]$ and volborthite $\text{Cu}_3\text{V}_2\text{O}_7(\text{OH})_2\cdot2\text{H}_2\text{O}$ $[3]$, are known as model systems for the spin-1/2 KAFM. They have slightly different kagome lattices of $\text{Cu}^{2+}$ ions. Herbertsmithite crystallizes in a rhombohedral structure with the space group $R\overline{3}m$, comprising an ideal arrangement of $\text{Cu}^{2+}$ ions in the kagome geometry, so as to be named a “structurally perfect kagome compound” $[2]$. Intensive experiments have established the absence of long-range order or spin glass transition down to 50 mK, suggesting a gapless or a very small spin-gapped range order, and approaches a large finite value at 60 mK, suggesting a gapless or a very small spin-gapped range order, and approaches a large finite value at 60 mK, suggesting a gapless or a very small spin-gapped range order, and approaches a large finite value at 60 mK, suggesting a gapless or a very small spin-gapped range order, and approaches a large finite value at 60 mK, suggesting a gapless or a very small spin-gapped range order, and approaches a large finite value at 60 mK, suggesting a gapless or a very small spin-gapped range order, and approaches a large finite value at 60 mK, suggesting a gapless or a very small spin-gapped range order, and approaches a large finite value at 60 mK, suggesting a gapless or a very small spin-gapped range order, and approaches a large finite value at 60 mK, suggesting a gapless or a very small spin-gapped range order, and approaches a large finite value at 60 mK, suggesting a gapless or a very small spin-gapped range order. The presence of these extrinsic contributions has made it difficult to determine the intrinsic ground state of the kagome lattice in herbertsmithite.

Another model system is volborthite $\text{Cu}_3\text{V}_2\text{O}_7(\text{OH})_2\cdot2\text{H}_2\text{O}$, which crystallizes in a monoclinic structure with the space group $C2/m$ $[7]$. There are two $\text{Cu}$ sites, namely, $\text{Cu}1$ and $\text{Cu}2$, in the kagome plane. Thus, the kagome lattice is slightly distorted, consisting of corner-shared isosceles $\text{Cu}1$-$\text{Cu}2$-$\text{Cu}2$ triangles, where the distances between two $\text{Cu}$ atoms are 3.03 Å ($\text{Cu}1$-$\text{Cu}2$) and 2.94 Å ($\text{Cu}2$-$\text{Cu}2$) $[5]$. This structural distortion should give rise to spatial anisotropy in $J$ in the kagome lattice, resulting in a $J1$-$J2$ kagome system rather than in a uniform one. The magnitude of the anisotropy has not yet been determined thus far, but was estimated to be less than 20% by theoretical analysis $[8]$. The kagome layers in volborthite are well separated by the $\text{V}_2\text{O}_7$ group and water molecules, resulting in a good two-dimensionality. Unlike herbertsmithite, volborthite does not suffer from such antisite disorder between $\text{Cu}^{2+}$ and $\text{Zn}^{2+}$ ions, because $\text{V}^{5+}$ ions cannot replace $\text{Cu}^{2+}$ ions: a mutual exchange between $\text{Cu}^{2+}$ and $\text{V}^{5+}$ ions is unfavorable in terms of ionic radius and Madelung energy. In spite of the strong antiferromagnetic interactions revealed by the large negative $\theta_W = -115$ K, volborthite shows no long-range magnetic order down to 60 mK, but exhibits a small spin glass transition at 1.1 K, which is likely caused by impurity spins $[9, 10]$. Magnetic susceptibility exhibits a broad maximum at $T \sim 0.25J/K_B$, indicative of the development of a short range order, and approaches a large finite value at 60 mK, suggesting a gapless or a very small spin-gapped (less than $J/1500$) ground state $[10]$. Very recently, a polycrystalline sample with much better quality has been prepared, and an intriguing phenomenon called “magnetization steps” was observed in magnetization curves at low temperatures $[10]$. However, it is still unclear whether these results on volborthite are intrinsic to the spin-1/2 KAFM or related to deviations from the ideal model. Therefore, it is necessary to search for alternative, more ideal kagome compounds in nature. In this letter, we report that vesignieite $\text{BaCu}_3\text{V}_2\text{O}_8(\text{OH})_2$
can be a suitable compound for realizing spin-1/2 KAFMs. The thermodynamic properties of vesignieite are studied and compared with those of the previous kagome compounds.

Vesignieite BaCu$_3$V$_2$O$_8$(OH)$_2$ is a natural mineral reported about a half century ago [11]. It crystallizes in a monoclinic structure of the space group $C2/m$ with lattice parameters of $a = 10.271$ Å, $b = 5.907$ Å, $c = 7.721$ Å and $\beta = 116.29^\circ$. This structure consists of Cu$_3$O$_6$(OH)$_2$ layers, made up of edge-shared CuO$_4$(OH)$_2$ octahedra and separated by VO$_4$ tetrahedra and Ba$^{2+}$ ions (Fig. 1 (a)). Cu$^{2+}$ ions form a nearly perfect kagome lattice, though there are two crystallographic sites for them, as in volborthite. The distortion of a Cu triangle from the regular one is negligible ($\sim 0.2\%$) with the distances between two Cu atoms being 2.962 Å (Cu1-Cu2) and 2.956 Å (Cu2-Cu2) [12]. Thus, the spatial anisotropy in $J$ may be much smaller than that in volborthite. Moreover, vesignieite is expected to be free of antisite disorder, the same as volborthite, because it contains no ions chemically similar to Cu$^{2+}$. From these structural and chemical features, we expect that vesignieite can be an ideal model system for the spin-1/2 KAFM to be compared with herbertsmithite and volborthite.

A polycrystalline sample of BaCu$_3$V$_2$O$_8$(OH)$_2$ was prepared by the hydrothermal method. 0.1 g of the mixture of Cu(OH)$_2$ and V$_2$O$_5$ in 3:1 molar ratio and 0.3 g of Ba(CH$_3$COO)$_2$ were put in a Teflon beaker placed in a stainless-steel vessel. The vessel was filled up to 60 volume % with H$_2$O, sealed and heated at 180 °C for 24 h. Sample characterization was performed by powder x-ray diffraction (XRD) analysis using Cu-Kα radiation. Magnetic and thermodynamic properties were measured in MPMS and PPMS (Quantum Design). All the peaks observed in the powder XRD pattern were indexed to reflections based on a monoclinic structure with the lattice constants $a = 10.273$ Å, $b = 5.907$ Å, $c = 7.721$ Å, $\beta = 116.29^\circ$ (Fig. 1 (b)), confirming that our sample is single-phase vesignieite [11][12]. The peaks are considerably broad, indicating a small particle size on the order of a few nm estimated using the Scherrer equation.

The temperature dependences of magnetic susceptibility $\chi$ and inverse susceptibility $\chi^{-1}$ of vesignieite are shown in Fig. 2 (a). $\chi^{-1}$ exhibits a linear temperature dependence above 150 K, interpreted as Curie-Weiss magnetism. A Curie-Weiss fit to the data between 200 and 300 K yields a moderately large negative $\theta_W = -77$ K and an effective moment $p_{eff} = 1.98 \mu_B$/Cu, which is slightly larger than the spin-only value expected for $S = 1/2$. The exchange coupling $J$ and Lande $g$-factor $g$ are estimated to be $J/k_B = 53$ K and $g = 2.16$, by
fitting the data between 150 and 300 K to the calculation for the spin-1/2 KAFM using the high-temperature-series expansion [13]. The $g$ of vesignieite is nearly equal to those of herbertsmithite ($g = 2.33$ [14] and volborthite ($g = 2.205$ [3], which are slightly larger than 2, reflecting a negative spin-orbit coupling constant for Cu$^{2+}$ ions. $J$ smaller than those of herbertsmithite ($J/k_B = 170$ K) [14] and volborthite ($J/k_B = 84$ K) [3] may be ascribed to the corresponding variation in Cu-O-Cu bond angle over the series: the smaller the bond angle, the larger the antiferromagnetic coupling.

We have observed neither a long-range order nor a spin glass transition down to 2 K in spite of the moderately strong antiferromagnetic interaction. The temperature dependence of $\chi$ under various fields shows no kink-like anomaly or thermal hysteresis between field cooling and zero-field cooling, as shown in Fig. 2 (b). The absence of long-range order is also supported by heat capacity $C$ measurements showing no peak-like anomaly indicative of a phase transition (Fig. 3). Thus, the geometrical frustration of the kagome lattice effectively suppresses long-range order down to low temperatures much less than $J/k_B$.

At low temperatures below $J/k_B = 53$ K, $\chi$ exhibits a slightly complicated temperature dependence. With decreaseing temperature, a small hump appears around 20 K, followed by a sharp rise below 10 K (Fig. 2 (a)). The latter must be due to the presence of nearly free impurity spins. Thus, $\chi$ should contain two independent contributions: $\chi_{\text{imp}}$ and $\chi_{\text{bulk}}$ from impurity and bulk spins, respectively. The former may be given as $\chi_{\text{imp}} = C_{\text{imp}}/(T - \theta_{\text{imp}})$, and should increase enormously as $T \rightarrow 0$. In contrast, the $T$ dependence of $\chi_{\text{bulk}}$ may be weak, compared with $\chi_{\text{imp}}$, at low temperatures. Thus, we fit the $\chi$ data between 2 and 7 K, assuming a $T$-independent term $\chi_0$ instead of $\chi_{\text{bulk}}$ (Fig. 2 (a)), we obtain $C_{\text{imp}} = 0.028$ cm$^{-3}$ K$^{-1}$ mol-Cu$^{-1}$, $\theta_{\text{imp}} = -1.7$ K, and $\chi_0 = 2.8 \times 10^{-3}$ cm$^3$ mol-Cu$^{-1}$. $C_{\text{imp}}$ indicates that 7% of spins behave as impurity spins. The presence of

impurity spins is also evidenced in the large field dependence of $\chi$ observed below 10 K (Fig. 2 (b)), as well as in the small but finite field dependence of $C/T$ (the inset of Fig. 3). The amount of impurity spins in vesignieite is larger than 0.07% for volborthite but smaller than 11% for herbertsmithite [10 [12], which were estimated by the same analysis on $\chi$. The origin of impurity spins in vesignieite is not clear but may be attributed to unidentified impurity phases or alien spins located near the surface of small particles or crystalline defects.

By subtracting $\chi_{\text{imp}}$ from $\chi$, we obtain the intrinsic magnetic susceptibility $\chi_{\text{bulk}}$, as shown in Fig. 2 (a). $\chi_{\text{bulk}}$ clearly exhibits a broad peak at 22 K $\sim 0.4 J/k_B$, and a substantially large value of $2.6 \times 10^{-3}$ cm$^3$ mol-Cu$^{-1}$ at $T = 2$ K. Note that this broad peak has already appeared as a hump or a shoulder in $\chi$ and has been observed by subtracting the extrinsic contribution of free spins. The broad peak indicates that short-range order develops remarkably below 22 K, and that the large finite value at the lowest temperature implies that the ground state is a gapless spin liquid, or, at least, that the gap is much smaller than $J/30$.

Let us discuss magnetic interactions in kagome lattices of the three Cu compounds in terms of orbital arrangements. It is common in all the three compounds that the degeneracy of the Cu 3d $e_g$ orbitals is lifted at room temperature owing to the Jahn-Teller distortion. However, the orbital arrangements are completely different from each other among the three compounds, as shown in Fig. 4 which can be deduced reasonably from the shape of octahedra around Cu$^{2+}$ ions. The $z^2$ orbital is occupied by an unpaired electron when two opposite Cu-O bonds are shorter than the other four bonds, while the $x^2 - y^2$ orbital is occupied when the two Cu-O bonds are longer than the others. In herbertsmithite, all the Cu$^{2+}$ ions have their unpaired electrons in the $x^2 - y^2$ orbital, which are placed symmetrically around the threefold axis, resulting in a structurally perfect kagome lattice [15]. In volborthite, on the other hand, the $x^2 - y^2$ orbital is responsible for the Cu2 site, while the $z^2$ orbital for the Cu1 site [15], which causes a disparity between $J_1$ (Cu1-Cu2) and $J_2$ (Cu2-Cu2). In contrast, a single orbital must be selected in vesignieite, as in the case of herbertsmithite, but it must be $z^2$ orbital instead of the $x^2 - y^2$ orbital orbital, giving rise to an essentially undistorted kagome network (Fig. 4). Nevertheless, the actual crystal symmetry is not trigonal but monoclinic, which comes from a lateral shift in the stacking of the kagome layers through intervening layers containing Ba$^{2+}$ ions and VO$_4$ tetrahedra. Since the distortion of Cu triangles in vesignieite is negligible, only 0.2%, one can consider vesignieite as a nearly ideal kagome system, which is better than volborthite from a structural point of view, and cleaner than herbertsmithite in terms of impurity spins.

Finally, we compare the $\chi_{\text{bulk}}$ for the three kagome compounds, in order to deduce the general feature of the KAFM. The temperature dependence of $\chi_{\text{bulk}}$ normalized by both $J$ and $g$ is shown in Fig. 5.
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herselvetime [15], respectively.

FIG. 4: Schematic representations of the arrangement of
Cu2+ orbitals in the kagome plane for three kagome com-
pounds. One of the two e_g orbitals, d_x^2−y^2 or d_z^2, carrying
spin-1/2 is depicted on each Cu atom.

FIG. 5: Temperature dependence of normalized
χ_{bulk} for vesignieite BaCu_3V_2O_8(OH)_2, volborthite
Cu_3V_2O_7(OH)_2·2H_2O and herbertsmithite ZnCu_3(OH)_6Cl_2.
The J/k_B and g used are 53 K and 2.16 for vesignieite,
84 K and 2.21 for volborthite [8], and 190 K and 2.23 for
herbertsmithite [15], respectively.

high temperature, all the curves tend to merge, as ex-
pected from the mean-field picture. However, they sep-
are from each other on cooling below T \sim 1.5 J/k_B
and show broad peaks at T_{peak} = 0.4 J/k_B for vesignieite
and 0.25 J/k_B for volborthite, indicative of the forma-
tion of short range order. Although the presence of such
a broad peak is not discernible for herbertsmithite, this
may be because of the experimental ambiguity in esti-
mating a large \chi_{imp} in \chi. In fact, in a recent NMR study
of herbertsmithite, it was found that local susceptibility
decided from shift measurements, which may be una-
fected by impurity spins or defects in the kagome plane,
shows similar broad maximum at around 0.4 J [16].
Therefore, T_{peak}, as well as the magnitude of \chi_{bulk}, is in
good agreement between vesignieite and herbertsmithite,
suggesting a general feature of the KAFM. In contrast,
the normalized \chi_{bulk} of volborthite seems considerably
different from the others: T_{peak} is lower, and the magni-
tude of \chi_{bulk} at T_{peak} is significantly larger. This is likely
due to the spatial anisotropy in J. Recent theoretical cal-
culations of \chi on a spin-1/2 spatially anisotropic Heisen-
berg model on the kagome lattice successfully reproduced
these tendencies with increasing anisotropy [17].

Common to all the three compounds, \chi_{bulk} seems to
approach a large finite value at T = 0, indicative of the absence of a spin gap having a realistic magni-
tude. Therefore, the intrinsic ground state of the spin-
1/2 KAFM must be a gapless spin liquid state or a state
with a gap much smaller than theoretically predicted [1].
This unusual ground state seems to be robust to the
spatial anisotropy of the kagome lattice, as observed in
volborthite. It is important to determine whether the anomalous magnetization steps that have recently been observed
in the high-quality sample of volborthite [10] are general features of the KAFM and are also observed
in vesignieite. To answer this question, a higher-quality sample with fewer impurity spins is required, and an ef-
fort to improve sample quality is in progress.

In conclusion, we have demonstrated that vesignieite
BaCu_3V_2O_8(OH)_2 is a spin-1/2 antiferromagnet on a
nearly ideal kagome lattice. The kagome lattice in ves-
nieite is more spatially isotropic than that in volborthite,
and contain fewer impurity spins than that in herbert-
smithite. The \chi_{bulk} of vesignieite shows a broad peak at
\sim 0.4 J/k_B due to short-range ordering and a large finite
value as T \rightarrow 0, without a long-range order, a spin glass
transition and a spin gap down to J/30. These features
are common to other kagome compounds, suggesting that
the ground state of the spin-1/2 KAFM is a very small
gapped or gapless spin liquid.

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