

Vesignieite: An $S = \frac{1}{2}$ Kagome Antiferromagnet with Dominant Third-Neighbor ExchangeD. Boldrin,^{1,*} B. Fåk,² E. Canévet,^{2,3} J. Ollivier,² H. C. Walker,⁴ P. Manuel,⁴ D. D. Khalyavin,⁴ and A. S. Wills¹¹*Department of Chemistry, University College London, 20 Gordon Street, London, WC1H 0AJ, United Kingdom*²*Institut Laue-Langevin, 71 avenue des Martyrs, CS 20156, 38042 Grenoble Cedex 9, France*³*Laboratoire de Physique des Solides, CNRS, Université Paris-Sud, Université Paris-Saclay, 91405 Orsay Cedex, France*⁴*STFC Rutherford Appleton Lab, ISIS Facility, Harwell Science and Innovation Campus, Didcot, OX11 0QX, United Kingdom*

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The spin- $\frac{1}{2}$ kagome antiferromagnet is an archetypal frustrated system predicted to host a variety of exotic magnetic states. We show using neutron scattering measurements that deuterated vesignieite $\text{BaCu}_3\text{V}_2\text{O}_8(\text{OD})_2$, a fully stoichiometric $S = 1/2$ kagome magnet with $< 1\%$ lattice distortion, orders magnetically at $T_N = 9$ K into a multi- \mathbf{k} coplanar variant of the predicted triple- \mathbf{k} octahedral structure. We find that this structure is stabilized by a dominant antiferromagnetic third-neighbor exchange J_3 with minor first- or second-neighbor exchanges. The spin-wave spectrum is well described by a J_3 -only model including a tiny symmetric exchange anisotropy.

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Geometrically frustrated magnets have the potential to host a multitude of exotic ground states, such as the elusive quantum spin liquid (QSL) states [1–3]. Having been studied theoretically for several decades, experimental progress has been hampered by a lack of model materials. However, recent experiments on new systems have revealed novel excitations and emergent phenomena beyond those originally predicted of both fundamental and technological interest [4–7]. The $S = 1/2$ kagome lattice is an archetypal frustrated system due to the combination of quantum spins and the low connectivity of its corner-sharing triangular lattice. Initial interest and understanding of this system focused on the nearest-neighbor (NN) Heisenberg Hamiltonian, as found experimentally in the well-studied herbertsmithite [8,9], spurred by the potential to realize various flavors of QSLs [10,11]. However, as most experimental realizations of the kagome antiferromagnet show deviations from a simple isotropic NN model, recent research has been extended to include exchange anisotropy and further-neighbor exchanges [12–14]. This has turned out to be equally interesting, with theory predicting novel types of magnetic order, such as octahedral and cuboc (cuboctahedral) structures for classical spins [14] and chiral or $U(1)$ spin liquids for quantum spins [15,16]. The vast majority of these theoretical predictions await experimental verification.

Model systems through which the effects of further-neighbor interactions can be explored in $S = \frac{1}{2}$ kagome magnets are rare. Kapellasite $\text{ZnCu}_3(\text{OH})_6\text{Cl}_2$ [17] and haydeeite $\text{MgCu}_3(\text{OH})_6\text{Cl}_2$ [18] are both members of the paratacamite mineral system shared by herbertsmithite, but they have ferromagnetic NN exchange. In the former, antiferromagnetic further-neighbor interactions drive the system into a chiral QSL state with fluctuations born from a

cuboc2 phase [15,17], while in the latter, antiferromagnetic further-neighbor interactions are again present but fail to drive the system away from the ferromagnetic ground state [18]. In volborthite, $\text{Cu}_3\text{V}_2\text{O}_7(\text{OH})_2 \cdot 2\text{H}_2\text{O}$, the distortion of the kagome lattice leads to inequivalent NN interactions and different local CuO_6 environments, suppressing long-range order to very low temperatures [19,20] and leading to a thermal Hall effect in the spin liquid state [21].

The mineral vesignieite $\text{BaCu}_3\text{V}_2\text{O}_8(\text{OH})_2$ [22] is a copper vanadate mineral similar to volborthite with a fully stoichiometric yet distorted $S = \frac{1}{2}$ kagome lattice, although this distortion is significantly less in the former, $< 1\%$ in terms of Cu—Cu distances. Given this comparison and considering the strong antiferromagnetic interactions inferred from the Weiss temperature $\theta_W \sim -80$ K and initial findings consistent with a quantum spin liquid state [23–27], it is surprising that vesignieite is now known to order magnetically at $T_N = 9$ K [28–31]. However, a more complete comparison of the system with both theory and related experimental systems requires determination of the magnetic structure and exchange interactions.

In this Letter, we use neutron scattering to determine the magnetic propagation vector \mathbf{k} and the magnetic excitation spectrum of vesignieite. We find that the material adopts an unconventional noncollinear multi- \mathbf{k} structure with the star $\mathbf{k} = \{1/2, 0, 0\}$, stabilized by a dominant antiferromagnetic third-neighbor J_3 interaction, see Fig. 1. We term this a hexagonal structure based on the nomenclature of the regular magnetic orders on the kagome lattice [14], see Fig. 1, and find it is closely related to the theoretically predicted noncoplanar octahedral structure.

Vesignieite consists of nearly perfect Cu^{2+} kagome layers that are separated by VO_4 tetrahedra and Ba^{2+} ions. Several crystallographic structural models have been

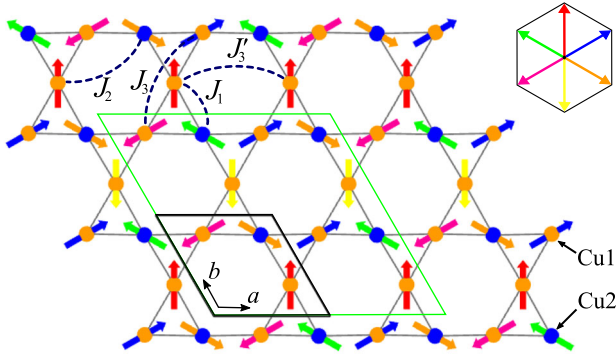


FIG. 1. The kagome lattice of vesignieite showing the two Cu^{2+} sites and the first four exchange interactions. The arrows on the Cu sites show the hexagonal magnetic structure with $\mathbf{k} = \{1/2, 0, 0\}$. In this structure, each moment, represented by the arrow color, has Fourier components associated with only a single \mathbf{k} vector. The black line is the crystallographic unit cell, and the green line is the magnetic unit cell. The inset illustrates how the spins point towards the vertices of a hexagon.

proposed [23,25,28–32]. The appearance of small satellite Bragg peaks in x-ray powder diffraction measurements in deuterated powder samples suggest the trigonal $P3_121$ space group (No. 152), where the tiny scalene distortion of the triangles corresponds to less than a 1% difference in the three Cu–Cu bond lengths [30]. The lowering of the kagome symmetry is due to a cooperative Jahn-Teller distortion and leads to the formation of two distinct Cu^{2+} sites as shown in Fig. 1, where the (orange) Cu2 site is orbitally disordered while the (blue) Cu1 site is orbitally ordered [30].

We used the fully deuterated $\text{BaCu}_3\text{V}_2\text{O}_8(\text{OD})_2$ single-phase powder samples of Ref. [30]. Magnetic susceptibility measurements show a negative value of $\theta_W = -75$ K [30], which is in good agreement with other vesignieite samples [23,25,28,30,31], and which suggests predominant antiferromagnetic interactions. However, attempts to estimate the strength and anisotropy of the exchange interactions based on nearest-neighbor exchange J_1 only [23,28,33] are bound to fail, as vesignieite has a dominant J_3 exchange, as we will show further below. Also, high-temperature series expansions for the kagome lattice [34] are not known for this particular case.

Our sample shows a clear antiferromagnetic phase transition in the magnetic susceptibility at $T_N = 9$ K [30] as in other high-quality powder samples [28,29]. A small zero-field-cooled or field-cooled splitting in the magnetic susceptibility [28–31] and a tiny hysteresis loop in the magnetization curve [28,30,31] suggest the formation of a weak ferromagnetic component with a magnitude of 1.6% of the staggered moment, possibly related to a minute spin canting within the kagome planes.

Neutron diffraction data collected on WISH at ISIS show weak additional Bragg peaks indicative of a magnetically ordered phase at $T = 1.5$ K when compared with the

paramagnetic phase at $T = 15$ K, see Figs. 2(a)–2(c), with an intensity corresponding to about $0.2 \mu_B$ on each Cu. Inelastic neutron scattering (INS) measurements on the time-of-flight spectrometer IN5 at the ILL also show such additional peaks at elastic energy transfers below T_N , see Fig. 2(d). A Pawley fit to the neutron diffraction data of Fig. 2(c) shows that these peaks, observed at Q values of $0.64, 1.08, \text{ and } 1.65 \text{ \AA}^{-1}$, can be indexed by a propagation vector of $\mathbf{k} = (1/2, 0, 0)$, which corresponds to the M point of the Brillouin zone of the kagome lattice.

The M point is of particular interest, as it characterizes the three regular triple- \mathbf{k} magnetic structures on the kagome lattice, namely the octahedral, cuboc1, and cuboc2 states [14]. These states can be distinguished by their extinction rules [14], and the observation of the three above mentioned Bragg peaks suggests that the magnetic structure of vesignieite is related to the octahedral state, which is favored by a large antiferromagnetic $J_3 > 0$ interaction and characterized by 90° rotations between neighboring spins [14]. The octahedral state is energetically degenerate with a number of coplanar states, such as the hexagonal

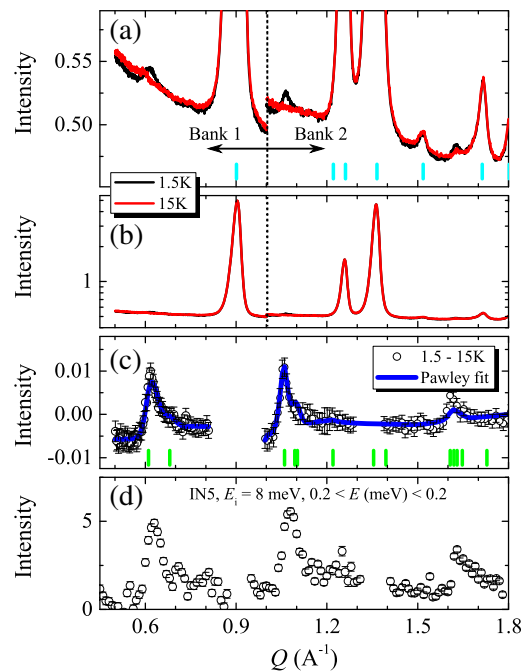


FIG. 2. Neutron diffraction data collected on banks 1 and 2 of the WISH diffractometer showing (a) weak magnetic Bragg peaks at $T = 1.5$ K (black) compared to $T = 15$ K (red) and (b) the full intensity scale. Blue tick marks indicate the nuclear reflections from the $P3_121$ crystal structure. The vertical dashed lines separate the data from banks 1 and 2. (c) Magnetic diffraction at $T = 1.5$ K after subtraction of the $T = 15$ K data fitted using a Pawley refinement (blue line). Green tick marks indicate the reflections from a magnetic structure based on $\mathbf{k} = (1/2, 0, 0)$. (d) Elastic line from INS data of the IN5 spectrometer at $T = 1.5$ K after the subtraction of $T = 30$ K data, showing the same three magnetic Bragg peaks.

(see Fig. 1), where neighboring spins are at 60° or 120° with respect to each other.

Inelastic neutron scattering measurements were performed on fully deuterated powder samples of weight between 2 and 7 g for temperatures $1.4 < T < 50$ K and incoming neutron energies $1.9 < E_i < 88$ meV using the MERLIN (ISIS) [35] and the IN4 and IN5 (ILL) [36] spectrometers. In the ordered phase, spin-wave excitations are observed with gapless modes emerging from the magnetic Bragg peak positions discussed above and a

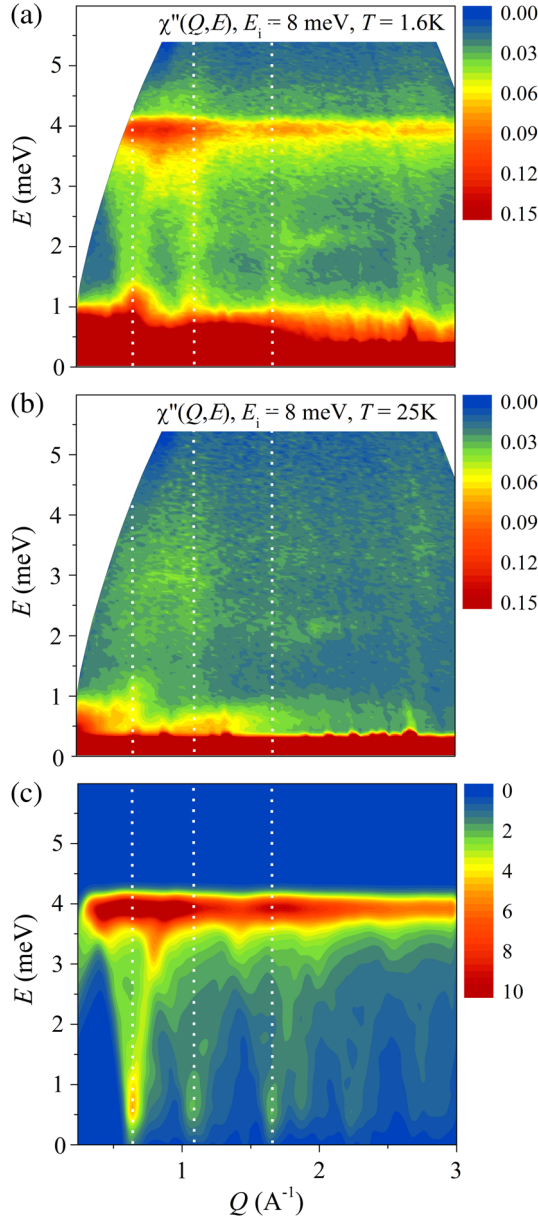


FIG. 3. Dynamic susceptibility $\chi''(Q, E)$ measured on IN5 with $E_i = 8.0$ meV at temperatures of (a) $T = 1.6$ K and (b) $T = 25$ K. (c) Spin-wave dispersion calculated within linear spin-wave theory with $J_3 = 1.9$ and $J'_3 = -0.1$ meV for an isotropic Hamiltonian. Dashed white lines are guides to the eye at $Q = 0.64, 1.08,$ and 1.64 \AA^{-1} .

strong flat band centered at an energy of 4 meV, see Fig. 3(a). These well-defined excitations have completely disappeared at temperatures well above T_N , see Fig. 3(b).

The data were modeled using semiclassical spin-wave theory [37] assuming the hexagonal magnetic structure of Fig. 1 and a spin Hamiltonian

$$\mathcal{H} = \sum_{i,j} J_{ij} [S_i^x S_j^x + S_i^y S_j^y + (1 + \delta) S_i^z S_j^z] + \mathbf{D}_{ij} \cdot (\mathbf{S}_i \times \mathbf{S}_j).$$

The flat mode at $E = 4$ meV fixes the main exchange integrals (here given in units of milli-electron volts) to $J_3 - J'_3 \approx 2.0$, whereas the width and the lack of dispersion of the flat mode impose $|J'_3| < 0.2$, $|J_1| < 0.1$, and $|J_2| \ll 0.1$. The best fit using an isotropic version of the above Hamiltonian ($\delta = 0$ and $\mathbf{D}_{ij} = 0$) was obtained with $J_3 = 1.9$ and $J'_3 = -0.1$; the powder-averaged calculation of this model is shown in Fig. 3(c). Identical results were obtained using the octahedral magnetic structure.

A J_3 dominant model in vesignieite is unexpected given the structural similarities to other $S = \frac{1}{2}$ kagome materials where NN exchange is dominant [8,17,18,38]. Jahn-Teller induced axial compression of the CuO_6 octahedra in vesignieite is due to a singly occupied $d_{x^2-y^2}$ orbital, meaning that both $\mu_3\text{-O(H)}$ and $\mu_2\text{-O}$ sites may be active in NN superexchange. The corresponding Cu–O–Cu angles range between 101° and 105° for the former, and between 78° and 89° for the latter [30,39,40]. These values lie on either side of the expected switchover from antiferro- to ferromagnetic superexchange according to the Goodenough-Kanamori-Anderson rules for copper oxides [41]. It is therefore conceivable that these competing paths cancel in vesignieite, leading to the negligible J_1 and dominant J_3 exchange energies we observe.

We will now discuss the hexagonal structure in more detail. It can be formed by projecting the octahedral structure onto two dimensions along the cubic [111] direction. It minimizes the J_3 -only antiferromagnetic Heisenberg Hamiltonian on the kagome lattice (along with a full continuum of magnetic orders including the octahedral and related coplanar and collinear orders), and it remains lowest in energy for $|J_i|$ up to about $|J_i| \lesssim J_3/2$ for $i = 1, 2, d$. It is a rather particular triple- \mathbf{k} structure: the Fourier components of a given arm of the star of $\mathbf{k} = \{1/2, 0, 0\}$ [i.e., $\mathbf{k}_1 = (1/2, 0, 0)$, $\mathbf{k}_2 = (0, 1/2, 0)$, or $\mathbf{k}_3 = (-1/2, -1/2, 0)$] are nonzero for only one site. In other words, each site has its own \mathbf{k} vector and its own Fourier component, and thus no coupling is expected between the ordered moments on the different sites. This is also clear from Fig. 1: an antiferromagnetic J_3 -only model results in three decoupled magnetic lattices. Introduction of a J'_3 interaction, the strongest “perturbation” in our case, does not couple these lattices either, but it induces some frustration for an antiferromagnetic J'_3 . In order to couple the three lattices, either J_1 or J_2 (the latter

negligible in our case) is needed, both of which are frustrating.

In such a “decoupled” multi- \mathbf{k} structure, disordering one of the sites will have no effect on the magnetic order nor on the magnetic excitations. This is exactly what happens in vesignieite, whereby the distortion leading to the rare $P3_121$ structural symmetry is a consequence of orbital disorder on the Cu2 site [30]. The partial orbital ordering occurs because the Cu^{2+} $d_{x^2-y^2}$ orbitals cannot be arranged symmetrically around the kagome triangles, unlike the superexchange mediating d_z orbitals in herbertsmithite [30]. Globally, the trigonal symmetry is retained via the 3_1 screw axis, which results in three kagome layers within each unit cell with adjacent layers rotated by 120° . Such a scenario is consistent with a multi- \mathbf{k} magnetic structure, where the screw axis can now be understood to arise from a “deselection” of different arms of the star of \mathbf{k} in each layer, i.e., the disordered site and its associated \mathbf{k} -vector changes in adjacent layers. A similar scenario is found in a partially ordered $S = 2$ kagome antiferromagnet [42], but the deduced single- \mathbf{k} magnetic structure is not consistent with either the trigonal symmetry or the dominant J_3 exchange of vesignieite, and it is not known which exchanges stabilize this structure.

Further evidence of a multi- \mathbf{k} structure in vesignieite is given by the observation of a small ferromagnetic component below T_N [30,31]. This component, which must be a secondary-order parameter, is only consistent with a multi- \mathbf{k} ground state. This general conclusion, which does not depend on the direction of the ferromagnetic component, comes from the requirement of time-reversal and translational invariance of the relevant free-energy coupling term. The invariance can only be achieved if the term involves a product of the magnetic order parameter components related to all three arms of the star of \mathbf{k} . Furthermore, magnetic susceptibility measurements on a single crystal sample indicate that the spins lie in the kagome plane [31]. The hexagonal structure is consistent with this finding and, unlike energetically degenerate collinear structures, it also satisfies the trigonal crystal symmetry. Unfortunately, the powder-averaged spin-wave spectra of the hexagonal structure cannot be distinguished within the experimental resolution from that of the noncoplanar octahedral structure.

We will now discuss the energetic stabilization of a coplanar, rather than noncoplanar, structure. The former is favored by a DM interaction on the strongest bond J_3 with the DM vector perpendicular to the kagome planes. This is allowed in the $P3_121$ space group, but such a DM interaction has no visible effect on the spin-wave spectrum, although it may explain the very weak ferromagnetic in-plane component inferred from magnetic susceptibility measurements [31]. A DM interaction on the J_1 bond would also have little effect, as J_1 is very weak in vesignieite. The tiny lattice distortion implies that the J_3

exchange along the Cu1–Cu2 chains could be slightly different from that along the Cu1–Cu1 chains, see Fig. 1. However, this leads only to minute changes in the spin-wave spectrum, even for differences as large as 20% between the two J_3 values.

Instead, we find the drive for coplanarity is a symmetric exchange anisotropy on J_3 , with the anisotropy term $\delta < 0$ in the above Hamiltonian. Such an anisotropy lifts one of the two “acoustic” branches to create a finite energy gap for that mode (the other mode remains gapless), and this introduces a strong spectral change in the powder average. We find evidence of such a gap in the low-energy dynamic susceptibility $\chi''(Q, E)$, see Fig. 4(a). Constant Q cuts of $\chi''(Q, E)$ at the acoustic branch $Q = 0.65 \pm 0.1 \text{ \AA}^{-1}$ reveal a significant reduction in intensity below $E \sim 0.5 \text{ meV}$, which is in excellent agreement with calculations performed with symmetric exchange anisotropy, see Fig. 4(b).

In conclusion, our neutron scattering data show that the mineral vesignieite orders magnetically at $T_N = 9 \text{ K}$ in a hexagonal multi- \mathbf{k} structure closely related to the octahedral structure predicted for the kagome lattice with dominant antiferromagnetic third-neighbor interactions, $J_3 > 0$. The measured spin-wave spectrum is also consistent with such a model. A particularity of this multi- \mathbf{k} structure, given that first- and second-neighbor interactions are weak compared to third-neighbor interactions, is that it consists of three essentially decoupled lattices, and is therefore insensitive to the orbital disorder of the Cu2 site of vesignieite. For a Heisenberg Hamiltonian, a dominating J_3 would stabilize a continuum of energetically equivalent magnetic structures, including the theoretically predicted regular octahedral state as well as nonregular coplanar or collinear states. In vesignieite, a weak symmetric exchange anisotropy of $\delta/J_3 = -0.006$ stabilizes the coplanar hexagonal magnetic structure from this manifold. To satisfy both the anisotropy and the trigonal crystal symmetry, neighboring spins are rotated by 60° or 120° and point towards the vertices of a hexagon. We note that the

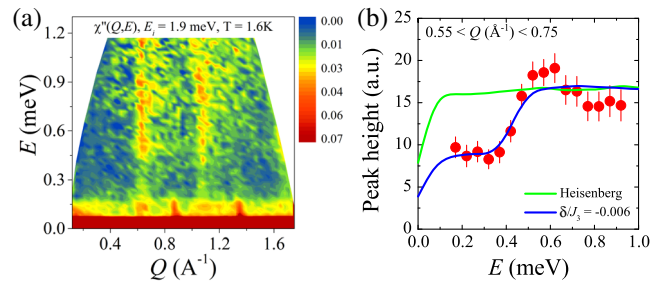


FIG. 4. (a) Dynamic susceptibility $\chi''(Q, E)$ measured on IN5 with $E_i = 1.9 \text{ meV}$ at $T = 1.6 \text{ K}$. (b) Energy scan of $\chi''(Q, E)$ at constant $Q = 0.65 \pm 0.1 \text{ \AA}^{-1}$, plotted with spin-wave calculations for a coplanar structure with $J_3 = 2 \text{ meV}$ for isotropic exchange (green curve) and symmetric exchange anisotropy $\delta/J_3 = -0.006$ (blue curve).

hexagonal structure can be thought of as three interlocked skewed square lattices, which extends the relevance of this system beyond its kagome geometry. The consequences these findings have on the recently predicted topological magnetic excitations in vesignieite remain to be seen [43].

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