Ferrimagnetic 120° magnetic structure in Cu$_2$OSO$_4$

Virgile Yves Favre,$^1$ Gregory S. Tucker,$^{1,2}$ Clemens Ritter,$^3$ Romain Sibille,$^2$ Pascal Manuel,$^4$ Matthias D. Frontzek,$^5$ Markus Kriener,$^6$ Lin Yang,$^{1,7}$ Helmut Berger,$^8$ Arnaud Magrez,$^8$ Nicola P. M. Casati,$^9$ Ivica Živković,$^{1,‡}$ and Henrik M. Rønnow$^{1,†}$

$^1$Laboratory for Quantum Magnetism, Institute of Physics, Ecole Polytechnique Fédérale de Lausanne, CH-1015 Lausanne, Switzerland
$^2$Laboratory for Neutron Scattering, Paul Scherrer Institut, CH-5232 Villigen PSI, Switzerland
$^3$Institute Laue Langevin, BP 156, 38042, Grenoble, France.
$^4$ISIS Facility, STFC Rutherford Appleton Laboratory, Oxfordshire OX11 0QX, UK
$^5$Neutron Scattering Division, Oak Ridge National Laboratory, Oak Ridge, Tennessee 37830, USA
$^6$RIKEN Center for Emergent Matter Science, Wako 351-0198, Japan.
$^7$Laboratory of Physics of Complex Matter, Institute of Physics, Ecole Polytechnique Fédérale de Lausanne, CH-1015 Lausanne, Switzerland
$^8$Crystal Growth Facility, Ecole Polytechnique Fédérale de Lausanne, Lausanne, Switzerland.
$^9$Swiss Light Source, Paul Scherrer Institut, 5232, Villigen, Switzerland

(Dated: October 9, 2020)

We report magnetic properties of a 3d$^9$ (Cu$^{2+}$) magnetic insulator Cu$_2$OSO$_4$ measured on both powder and single crystal. The magnetic atoms of this compound form layers, whose geometry can be described either as a system of chains coupled through dimers or as a Kagomé lattice where every 3rd spin is replaced by a dimer. Specific heat and DC-susceptibility show a magnetic transition at 20 K, which is also confirmed by neutron scattering. Magnetic entropy extracted from the specific heat data is consistent with a $S = 1/2$ degree of freedom per Cu$^{2+}$, and so is the effective moment extracted from DC-susceptibility. The ground state has been identified by means of neutron diffraction on both powder and single crystal and corresponds to a ~120 degree spin structure in which ferromagnetic intra-dimer alignment results in a net ferrimagnetic moment. No evidence is found for a change in lattice symmetry down to 2 K. Our results suggest that Cu$_2$OSO$_4$ represents a new type of model lattice with frustrated interactions where interplay between magnetic order, thermal and quantum fluctuations can be explored.

I. INTRODUCTION

Materials with antiferromagnetic Heisenberg interactions between spins on a triangular lattice$^{[1,2]}$ inherently exhibit large frustration, resulting in many similar energy states giving rise to novel behavior. In practice, there exist several ways to build a full lattice from triangular motifs. The notion of quantum spin liquid was introduced in the form of the Resonating Valence Bond, as a potential ground state of other triangle-containing lattice geometries than the pure triangular and Kagomé lattices. In our context we present the study of Cu$_2$OSO$_4$,$^{[30]}$ which hosts a quasi-2D lattice built from triangular motifs. One way to describe the lattice is that of a Kagomé lattice with one third of the sites replaced by $S = 1/2$ pairs (dimers). Another way to characterize it would be chains coupled through spin pairs in a triangular frustrated pattern. As shall be presented below, the spin-pair appear ferromagnetically aligned, such that an effective model for the system could be described as a Kagome lattice with $S = 1/2$ on 2/3 of the sites and $S = 1$ on 1/3 of the sites. No single crystal growth of Cu$_2$OSO$_4$ has previously been reported$^{[31]}$. Studies of powder samples of Cu$_2$OSO$_4$ reported the DC susceptibility of the compound and showed evidence of a transition to a magnetically long range ordered state at 20 K. The DM interaction in the sample was estimated by the means of Electron Spin Resonance (ESR)$^{[25]}$. From bulk measurements, a non-collinear antiferromagnetic ground state was proposed$^{[32]}$. Here we report single crystal growth and the details of the ground state of Cu$_2$OSO$_4$, derived from DC-susceptibility, magnetization, heat capacity, as well as x-ray and neutron scattering.
II. EXPERIMENTAL DETAILS

Single crystals of Cu$_2$OSO$_4$ were grown by chemical vapor transport. High quality Cu$_2$OSO$_4$ powder was synthesized using anhydrous CuSO$_4$ as a source in a quartz crucible placed in the center of a muffle furnace and heated at 740 °C. Two different transport agents were placed in a quartz ampoule at room temperature: Cl$_2$ and NiBr$_2$, as well as a portion of the Cu$_2$OSO$_4$ powder. The ampoules were placed in a two zone gradient furnace. The best charge and growth-zone temperatures were 650 °C and 550 °C respectively. After five weeks, several dark-brown, semitransparent crystals were obtained. The typical dimensions of the crystals are 4x2x0.5 mm$^3$. On most of the crystals the b axis can be identified as an edge and most of them also present a (001) facet.

Specific heat was measured using a physical properties measurement system (PPMS, Quantum Design, Inc) and magnetization was measured using both PPMS and a magnetic properties measurement system (MPMS, Quantum Design, Inc). Neutron diffraction experiments were performed on WAND, ZEBRA, D20 and WISH beam lines at ORNL, PSI, ILL and ISIS respectively. The measurement on D20 was done using the high resolution option with takeoff angle 90° and a wavelength of 2.41 Å. 4 hour measurements were taken at 1.5 K and at 30 K while the temperature ramp was done between 1.5 K and 30 K using 30 min runs with about 0.45 K between consecutive runs. Synchrotron x-ray diffraction was performed at the MS-X04SA beam line at SLS, PSI. For powder diffraction, crushed single crystals were used to minimize impurities.

III. RESULTS

A. X-ray diffraction and crystal structure

According to a previous study, the compound belongs to the monoclinic space group C 2/m with lattice parameters a = 9.355(10) Å, b = 6.312(5) Å, c = 7.628(5) Å, α = γ = 90°, and β = 122.29°.

To determine the temperature dependence of the nuclear structure, we performed temperature dependent x-ray diffraction on a powder sample. The temperature dependence of lattice parameters was extracted from LeBail fits (LBF) and is shown in Fig. 1 as well as the unit cell volume. The overall thermal contraction of the lattice has been observed down to 50 K, with a minimum of lattice parameters a and b around 60 K. This non-monotonic temperature dependence could be due to the onset of magnetic correlations coupling to the lattice. Similar magneto-elastic coupling is observed below the ordering temperature (Fig. 2).

The crystal structure of Cu$_2$OSO$_4$ gives rise to an interesting magnetic lattice. The copper atoms occupy two inequivalent positions. They are arranged in the ab-plane, with atoms on copper site one (Cu$_1$) exactly in the plane, while atoms of copper site two (Cu$_2$) are positioned symmetrically above and below the plane. Fig. 3(a) shows how the planes are then interconnected through SO$_4$ tetrahedra. The arrangement of Cu$_1$ and Cu$_2$ ions in the quasi-2D planes can be described either as

![FIG. 1. Change in lattice parameters and unit cell volume obtained from LeBail fitting of powder x-ray diffraction data.](attachment:image.png)

Cu$_1$ chains along the crystallographic b-axis, interconnected by Cu$_2$ dimers in a frustrated zig-zag pattern; or it can be described as a Kagomé lattice with one third of the sites replaced by dimers, or it can be viewed as Cu$_1$ chains coupled through Cu$_2$ dimers. Fig. 3(b) illustrate how viewing the magnetic layers rotated 8.5° around the b-axis plane overlays the Cu$_2$ ions resulting in the familiar Kagomé motif. Fig. 9 show the magnetic lattice viewed directly along c$^\ast$.

B. Specific Heat

The specific heat $C_p$ measured from 2 K to 200 K in zero field and in a magnetic field of 9 T is shown in Fig. 4. The $C_p$ above 70 K for both fields is essentially the same, increas-
FIG. 2. Relative changes in lattice parameters obtained from neutron diffraction. The data has been normalized to data measured at 29 K (black square).

(a) View from the b axis, showing a slice of the Kagomé-like planes formed by copper atoms in Cu$_2$OSO$_4$, highlighting the SO$_4$ tetrahedra connecting the copper planes.

(b) Kagomé-like planes formed by copper atoms in Cu$_2$OSO$_4$ in the ab-plane. The two colors correspond to two inequivalent copper sites.

FIG. 3. Cu$_2$OSO$_4$ structure obtained from X-ray diffraction.

ing monotonically with increasing temperature. In zero field a pronounced peak is found at 20 K, corresponding to a transition into a magnetically long range-ordered phase, as evidenced by other experimental measurements discussed in later sections. The peak shifts to slightly higher temperature at 9 T. In order to extract the magnetic part of the specific heat, C$_{mag}$, and to deduce the corresponding entropy $S_{mag}$, we simulate the lattice contribution from the high temperature data by taking into account one Debye ($C_D$) and several Einstein ($C_{E,i}$) contributions. We use a combined fit to describe the $C_p$ and the volume of the unit cell obtained from x-ray diffraction by a phonon (lattice only) model. Similarly to what has been done in [40, 41], the lattice contribution to the specific heat is given by $C_p = C_D + \sum_i C_{E,i}$ with:

$$C_D = 9n_D R \left( \frac{T}{\Theta_D} \right)^3 \int_0^{\Theta_D/T} \frac{x^4 e^x}{(e^x - 1)^3} dx$$

$$C_E = 3n_E R \frac{y^2 e^y}{(e^y - 1)^2}, y = \frac{\Theta_E}{T}$$

Where R denotes the gas constant, $\Theta_D$ and $\Theta_E$ are the Debye and Einstein temperatures respectively. The sum $n_D + n_E$ is the total number of atoms per formula unit. The volume of the unit cell has been fitted together with the specific heat using the Debye and Einstein contributions to the internal energy. The volume of the unit cell is related to the internal energy by:

$$V(T) = \gamma U(T)/K_0 + V_0$$

Where $V_0$ is the cell volume at $T = 0$ K, $K_0$ is the bulk modulus and $\gamma$ is the Grüneisen parameter. $U(T)$ is the internal energy which can be expressed in terms of the Debye and Einstein approximation as:

$$U(T) = U_D(T) + U_E(T)$$

$$U_D(T) = 9n_D k_B T \left( \frac{T}{\Theta_D} \right)^3 \int_0^{\Theta_D/T} \frac{x^3 e^x}{e^x - 1} dx$$

$$U_E(T) = \frac{3}{2} k_B \sum_i n_{E,i} \Theta_{E,i} \coth \left( \frac{\Theta_{E,i}}{2T} \right)$$

The best fit for both sets of data, using one Debye branch and two Einstein branches yields the characteristic temperatures: $\Theta_D = 171$ K, $\Theta_{E1} = 245$ K and $\Theta_{E2} = 939$ K with $n_D = 1$, $n_{E1} = 3$ and $n_{E2} = 4$. This fit was performed using data for temperatures larger than 70 K. The volume of the unit cell at zero Kelvin has also been fitted to be: $V_0 = 373.65 \text{ Å}^3$, (Fig. [1].)

Fig. 4 show the resulting $C_{mag}/T$ in zero field as well as the magnetic entropy, $S_{mag}(T)$ obtained by integrating $C_{mag}/T$ over temperature. The magnetic entropy saturates around 101(19)% of $R \ln 2$ per formula unit, which is in agreement
with the entropy of a two level spin half system. A similar analysis carried out on the 9 T data (not shown) indicates negligible field effects. The magnetic entropy is shared between short range correlations (Fig. 4, green shading) and phase transition to long range order (Fig. 4, blue shading). We estimate that 18(5)% of the magnetic entropy contributes to the phase transition.

**C. Susceptibility and magnetization**

The inverse DC susceptibility measured on a single crystal, with a field of 0.1 T, pointing along the three relevant crystallographic directions: a, b, and c* is shown in Fig. 5. The high temperature part of $\chi(T)$ fits the Curie-Weiss law, $\chi(T) = C/(T-\Theta_{CW}) + \chi_0$, where $\Theta_{CW}$ is the Curie-Weiss temperature, $C = \mu_{eff}^2 / 8$ and $\chi_0$ a temperature independent diamagnetic and background term. $\mu_{eff} = g\sqrt{S(S+1)}$ is the effective magnetic moment, which is temperature independent. For a spin half system with a Landé g-factor of 2 the effective magnetic moment is worth approximately 1.7 $\mu_B$. Deviations from this value can be explained by either a slightly different spin state or a g-factor different from 2, also possibly anisotropic. The fitted effective moments, $\Theta_{CW}$ and $\chi_0$ are given in Table I and the corresponding fits can be observed in Fig. 5. The Curie Weiss temperature is isotropic within errorbars and negative, which indicate dominating antiferromagnetic interactions. The g-tensor is slightly anisotropic with easy axis along b and hard axis along a. Below 20K the susceptibility steeply increases indicating a magnetic transition into a state with a ferromagnetic component. ZFC - FC splitting at low temperature is typical of weak ferromagnetic hysteresis. The magnetic transition occurring well below $\Theta_{CW}$ indicates order is suppressed by fluctuations due to a combination of low dimensionality and frustration.

**Fig. 5.** Curie-Weiss fits of the high temperature susceptibility data, along the a axis (blue), b axis (red), and c* axis (yellow). The red lines indicate the fit for each direction.

| direction | $\Theta_{CW}$ [K] | $\chi_0$ | $\mu_{eff}$ [$\mu_B$] |
|-----------|------------------|---------|-----------------------|
| a         | -71(4)           | 5.4e-05 | 1.91(25)              |
| b         | -75(1)           | 4.7e-04 | 2.23(25)              |
| c*        | -70(1)           | -7.6e-05 | 2.11(11)             |

**TABLE I.** Results of Curie-Weiss fits for measurements along a, b and c*
D. Neutron Diffraction

To determine the magnetic structure, neutron diffraction measurements were performed on powder samples. Fig. 8 shows in blue the data measured at 1.5 K. The magnetic scattering has been separated by measuring a powder diffraction pattern above the magnetic transition at 30 K. The subtraction of the nuclear data from the base temperature data is displayed in red in Fig. 8. Some up-down features appear due to lattice contraction, changing the Bragg peaks positions.

Every magnetic contribution is located at a nuclear Bragg peak. This indicates that the magnetic propagation vector is k=(000). Magnetic symmetry analysis was done for this propagation vector using the program BasIreps for the Wykoff sites 42 (Cu$_1$) and 4i (Cu$_2$) in space group C2/m. Table II lists the allowed irreducible representations (Irreps) labelled $\Gamma_1 \rightarrow \Gamma_4$ and their basis vectors labelled (u,v,w) for site 1 and (r,s,t) for site 2 and shows how the magnetic moments on the symmetry related sites x,y,z and -x,y,-z are constrained and transformed by the different possible Irreps. Refinements were carried out using the Fullprof suite. The 30 K data were first refined to solve the nuclear structure. The scale factor obtained in this refinement was then fixed and used to refine the purely magnetic scattering of a dataset created by subtracting the 30 K data from the 1.5 K data having the same statistics. In doing so, the sensitivity for the magnetic contribution increases strongly reducing the uncertainties in the determination of the magnetic components.

TABLE II. Basis functions of irreducible representations $\Gamma_\nu$ for k = (000). Only the real components are presented because the imaginary part is zero. The two equivalent copper sites are related through the indicated transformations.
In addition to the powder diffraction we also carried out a single crystal neutron diffraction experiment on the four-circles diffractometer ZEBRA, at SINQ, PSI. The crystal used turned out to present a strong mosaicity, which did not enable us to collect intensity at Bragg reflections in a systematic way and in all the directions of reciprocal space. Intensities for a set of 55 reflections were collected at a base temperature of 1.5 K as well as at 25 K to solve the nuclear structure. The result of the fit of the experimental data is presented in the inset of Fig. 8 for a choice of Irrep $\Gamma_1$ on both copper sites. The best refinement is given by $\Gamma_1$ on both inequivalent sites. Fig. 9 shows in purple the result of the calculation of the base temperature data using the fit result. Fig. 9 shows the associated configuration of magnetic moments. The result of the fit of irreducible representation $\Gamma_1$ on both sites is presented in table III. If the Irreps are set to the result obtained by the powder diffraction experiment, then the free parameters in the single crystal refinement from Zebra can be reasonably adjusted and lead to a magnetic structure showing good agreement with the one obtained from the refinement of the powder data. The magnetic structure consists of Cu$_1$ antiferromagnetic chains with non colinear moments. This is the configuration that a 1D chain would adopt in magnetic field along the chain, with the field strength equal to half the saturation field. The chains are connected by Cu$_2$ dimers. The Cu$_2$ atoms in the dimer are ferromagnetically coupled. The copper atoms in the chains form an approximate 120 degrees structure with 4 spins: two Cu$_2$ atoms and two Cu$_1$ atoms belonging to the Cu$_1$ chains. The magnetic moments along the a and $c^*$ directions are compensated and the magnetic structure only supports a net moment along the b axis. Using values obtained from neutron diffraction in table III, we obtain the following saturation moment along the b axis: 0.23(3) $\mu_B$. This moment is made up of a quarter of the sum of the moments of two Cu$_1$ and two Cu$_2$ atoms, and is in perfect agreement with the isothermal magnetization shown in Fig. 7.

Temperature dependent neutron diffraction was performed on a powder sample. Using LBF, one can extract the associated change of the lattice parameters on the whole measured range. Fig. 2 shows the relative change of the lattice parameters, which reflect the onset of magnetic order below 20 K. Fig. 10 shows the evolution of the ordered magnetic moments as a function of temperature, obtained from neutron diffraction. Solid lines correspond to power-law fits: $\mu(T) \propto (T_N - T)^{2\beta}$. The fit of the data yields $T_N = 19.7$ (07) K, shared by the two sites, and $\beta = 0.12(1)$ for site 1 and $\beta = 0.13(2)$ for site 2.
IV. DISCUSSION

The ordered structure determined from the neutron powder diffraction is fully consistent with exchange paths present in this compound. A close inspection of the structure reveals which are the most relevant superexchange paths. The pathway between two Cu$_2$ ions contains oxygen ions, forming the Cu$_2$ - O - Cu$_2$ angle $\sim 93.0^\circ$ which favors a ferromagnetic $J_{22}$ according to the Goodenough-Kanamori-Anderson (GKA) rules. On the other hand the Cu$_1$ - O - Cu$_1$ angle between two nearest-neighbor Cu$_1$ atoms is 114.9$^\circ$. This falls well in the range of values predicted by GKA rules to favor antiferromagnetic $J_{11}$ interactions. For the coupling between two inequivalent copper sites there are two distinct superexchange paths, one forming a Cu$_1$ - O - Cu$_2$ angle of 104.9$^\circ$ while the other one is 117.3$^\circ$. Such values are again consistent with antiferromagnetic couplings ($J_{21a}$ and $J_{21b}$, respectively).

Additional exchange pathways exist and involve sulphur tetrahedra, more precisely Cu - O - O - Cu super-super-exchange interactions. They provide a coupling between Cu$_2$ dimers as well as an overall inter-planar coupling which eventually leads to the observed long-range order. It is a non-trivial task to estimate their relative strength to super-exchange in-plane coupling. Future inelastic neutron scattering experiments and modelling of dispersion relations could give us an indication which interactions are the most relevant for the long-range order in Cu$_2$ - O - Cu$_2$.

As a final note, an antisymmetric Dzyaloshinskii-Moriya (DM) interaction has been indicated to exist in this compound$^{[3]}$, compatible with crystal symmetry. Its magnitude has been estimated to be $D \sim 7$ K. If we take $\theta_{CW} \sim 70$ K as an estimate for $J$, we arrive at $D/J \gtrsim 0.1$. For the Kagomé lattice, DM interactions have been predicted to cause a quantum phase transition stabilizing 120$^\circ$ order above $D_c = 0.1^{[21,22]}$. Given the similar relative order of $D$ in Cu$_2$OSO$_4$, it is possible that this interaction is partly responsible for the 120$^\circ$ order and as a consequence Cu$_2$OSO$_4$ may be close to a quantum phase transition, which could possibly be reached by tuning the system through pressure or chemical substitution.

V. CONCLUSION

In summary, we have presented a detailed study of the magnetic properties of Cu$_2$OSO$_4$. We confirmed that the structure of Cu$_2$OSO$_4$ does not change upon cooling and that the ground state corresponds to a $S = 1/2$ system. The Curie Weiss temperatures give an idea of the order of magnitude of the magnetic couplings involved in the system, 70 K, however, the system undergoes a second order magnetic phase transition to a magnetically long range ordered state only below 20 K. Neutron scattering reveals that the ground state corresponds roughly to 120$^\circ$ order. The fact that this specific magnetic structure turns out to be the ground state, even though one third of the sites in the Kagomé-like lattice is replaced by ferromagnetic dimers is interesting. The rather small entropy linked to the transition suggest that there might be interesting dynamics related to the formation of ferromagnetic pairs and 120$^\circ$ triangles and subsequent alignment of these units. We hope this study will stimulate further theoretical and experimental studies of the dynamics in this new triangular motif model compound.

VI. ACKNOWLEDGMENTS

V. Y. F. thanks P. Babkevich for his help with the refinement of diffraction data, and F. Mila for stimulating discussions. We acknowledge the Paul Scherrer Institut, Villigen, Switzerland for provision of synchrotron radiation beamtime at beamline MS-X04SA of the SLS. This work is partially based on experiments performed at the Swiss spallation neutron source SINQ, Paul Scherrer Institute, Villigen, Switzerland, at the STFC ISIS Facility$^{[21]}$ and at the Institut Laue-Langevin$^{[22]}$. A portion of this research used resources at the High Flux Isotope Reactor, a DOE Office of Science User Facility operated by the Oak Ridge National Laboratory. This work was supported by the Swiss National Science Foundation (SNSF) grant No. 188648.

---

1. A. Olariu, P. Mendels, F. Bert, B. G. Ueland, P. Schiffer, R. F. Berger, and R. J. Cava, “Unconventional Dynamics in Triangular Heisenberg Antiferromagnet NaCrO 2,” Physical Review Letters, vol. 97, Oct. 2006.
2. Y. Shirata, H. Tanaka, A. Matsuo, and K. Kindo, “Experimental Realization of a Spin-1/2 Triangular-Lattice Heisenberg Antiferromagnet,” Physical Review Letters, vol. 108, Jan. 2012.
3. Y. Kojima, M. Watanabe, N. Kurita, H. Tanaka, A. Matsuo, K. Kindo, and M. Avdeev, “Quantum magnetic properties of the spin-1 2 triangular-lattice antiferromagnet Ba 2 La 2 CoTe 2 O 12,” Physical Review B, vol. 98, Nov. 2018.
4. P. Anderson, “Resonating valence bonds: A new kind of insulator?,” Materials Research Bulletin, vol. 8, no. 2, pp. 153 – 160, 1973.
5. P. Fazekas and P. W. Anderson, “On the ground state properties of the anisotropic triangular antiferromagnet,” Philosophical Magazine, vol. 30, pp. 423–440, Aug. 1974.
6. M. Collins and O. Petrenko, “Triangular antiferromagnets. Can J Phys 75:605,” Canadian Journal of Physics, vol. 75, pp. 605–, 09 1997.
7. F. Ferrari, A. Parola, S. Sorella, and F. Becca, “Dynamical structure factor of the $J_1$ - $J_2$ Heisenberg model in one dimension: The variational Monte Carlo approach,” Physical Review B, vol. 97, June 2018.
M. Hermele, Y. Ran, P. A. Lee, and X.-G. Wen, “Properties of an spin-liquid-like state in a spin-1/2 square-lattice antiferromagnet perovskite induced by d-0 d-0 cation mixing,” *Nature communications*, vol. 9, no. 1, p. 1085, 2018.

M. P. Shores, E. A. Nytko, B. M. Bartlett, and D. G. Nocera, “A Structurally Perfect $S = 1 / 2$ Kagomé Antiferromagnet,” *Journal of the American Chemical Society*, vol. 127, pp. 13462–13463, Oct. 2005.

P. Mendels and F. Bert, “Quantum kagome frustrated antiferromagnets: One route to quantum spin liquids,” *Comptes Rendus Physique*, vol. 17, pp. 455–470, Mar. 2016.

J. S. Helton, K. Matan, M. P. Shores, E. A. Nytko, B. M. Bartlett, Y. Yoshida, Y. Takano, A. Suslov, Y. Qiu, J.-H. Chung, D. G. Nocera, and Y. S. Lee, “Spin Dynamics of the Spin-1/2 Kagome Lattice Antiferromagnet ZnCu$_3$ (OH)$_6$ Cl$_2$,” *Physical Review Letters*, vol. 98, Mar. 2007.

A. Zorko, S. Nellutla, J. van Tol, L. C. Brunel, F. Bert, F. Duc, J.-C. Trombe, M. A. de Vries, A. Harrison, and P. Mendels, “Dzyaloshinsky-Moriya Anisotropy in the Spin-1/2 Kagome Compound ZnCu$_3$ (OH)$_6$ Cl$_2$,” *Physical Review Letters*, vol. 101, July 2008.

S. Depenbrock, I. P. McCulloch, and U. Schollwock, “Nature of the Spin-Liquid Ground State of the $S = 1 / 2$ Heisenberg Model on the Kagome Lattice,” *Physical Review Letters*, vol. 109, Aug. 2012.

F. Mila, “Low-Energy Sector of the $S = 1 / 2$ Kagome Antiferromagnet,” *Physical Review Letters*, vol. 81, pp. 2356–2359, Sept. 1998.

R. R. P. Singh and D. A. Huse, “Ground state of the spin-1/2 kagome-lattice Heisenberg antiferromagnet,” *Physical Review B*, vol. 76, Nov. 2007.

S. Yan, D. A. Huse, and S. R. White, “Spin-Liquid Ground State of the $S = 1/2$ Kagome Heisenberg Antiferromagnet,” *Science*, vol. 332, no. 6034, pp. 1173–1176, 2011.

S. Depenbrock, I. P. McCulloch, and U. Schollwock, “Nature of the Spin-Liquid Ground State of the $S = 1/2$ Heisenberg Model on the Kagome Lattice,” *Physical Review Letters*, vol. 109, Aug. 2012.

M. Hermele, Y. Ran, P. A. Lee, and X.-G. Wen, “Properties of an algebraic spin liquid on the kagome lattice,” *Physical Review B*, vol. 77, June 2008.

L. Clark, J. C. Orain, F. Bert, M. A. De Vries, F. H. Aidoudi, R. E. Morris, P. Lightfoot, J. S. Lord, M. T. F. Telling, P. Bonville, J. P. Attfield, P. Mendels, and A. Harrison, “Gapless Spin Liquid Ground State in the $S = 1/2$ Vanadium Oxyfluoride Kagome Antiferromagnet [NH$_4$]$_2$ [C 7 H 14 N] [ V 7 O 6 F 18 ],” *Physical Review Letters*, vol. 110, May 2013.

Y. Izňal, F. Becca, S. Sorella, and D. Poilblanc, “Gapless spin-liquid phase in the kagome spin-1/2 Heisenberg antiferromagnet,” *Physical Review B*, vol. 87, Feb. 2013.

M. Fu, T. Imai, T.-H. Han, and Y. S. Lee, “Evidence for a gapped spin-liquid ground state in a kagome Heisenberg antiferromagnet,” *Science*, vol. 350, no. 6261, pp. 655–658, 2015.

M. Takano, T. Shinjo, and T. Takada, “On the spin arrangement in kagome lattice of antiferromagnetic $kF_1$ 1$\bar{1}$(OH)$_{6}$(SO$_4$)$_2$,” *Journal of the Physical Society of Japan*, vol. 30, no. 4, pp. 1049–1053, 1971.

Y. Okamoto, H. Yoshida, and Z. Hiroi, “Vesignieite BaCu$_3$ V$ _2$ O$_8$(OH)$_2$ as a Candidate Spin-1/2 Kagome Antiferromagnet,” *Journal of the Physical Society of Japan*, vol. 78, p. 033701, Mar. 2009.

T. H. Han, J. S. Helton, S. Chu, A. Prodi, D. K. Singh, C. Mazzoli, P. Müller, D. G. Nocera, and Y. S. Lee, “Synthesis and characterisation of single crystals of the spin-1/2 kagome-lattice antiferromagnets $\text{Zn}_x\text{Cu}_{4-x} \text{(OH)}_4 \text{Cl}_2$,” *Physical Review B*, vol. 83, Mar. 2011.

B. Martínez, F. Sandiumenge, A. Rouco, A. Laburta, J. Rodríguez-Carvajal, M. Tovar, M. Causa, S. Galí, and X. Obradors, “Magnetic dilution in the strongly frustrated kagome antiferromagnet SrGa$_2$ x Cr$_x$ O$_9$,” *Physical Review B*, vol. 46, pp. 10786–10792, Nov. 1992.

Z. Hiroi, M. Hanawa, N. Kobayashi, M. Nohara, H. Takagi, Y. Kato, and M. Takigawa, “Spin-1/2 kagome-like lattice in volatilethite cu$_{13}$V$_2$O$_{7}$(OH)$_{2}$H$_2$O,” *Journal of the Physical Society of Japan*, vol. 70, no. 11, pp. 3377–3384, 2001.

P. Mendels and F. Bert, “Quantum Kagome Antiferromagnet ZnCu$_3$(OH)$_6$ Cl$_2$,” *Journal of the Physical Society of Japan*, vol. 79, p. 011001, Jan. 2010.

M. Wolf and K. D. Schotte, “Ising model with competing next-nearest-neighbour interactions on the Kagome lattice,” *Journal of Physics A: Mathematical and General*, vol. 21, pp. 2195–2209, may 1988.

O. Cépas, C. M. Fong, P. W. Leung, and C. Luillier, “Quantum phase transition induced by Dzyaloshinskii-Moriya interactions in the kagome antiferromagnet,” *Physical Review B*, vol. 78, Oct. 2008.

Y. Huh, L. Fritz, and S. Sachdev, “Quantum criticality of the kagome antiferromagnet with Dzyaloshinskii-Moriya interactions,” *Physical Review B*, vol. 81, Apr. 2010.

B. Dalla Piazza, M. Mourigal, N. B. Christensen, G. J. Nilsen, P. Tregenna-Piggott, T. G. Perring, M. Enderle, D. F. McMorrow, D. A. Ivanov, and H. M. Rønnow, “Fractional excitations in the square-lattice quantum antiferromagnet,” *Nature Physics*, vol. 11, pp. 62–68, Jan 2015.

E. Flügel-Kahler, “Die Kristallstruktur von Dolerophanit, Cu$_2$(SO$_4$)$_3$,” *Acta Crystallographica*, vol. 16, pp. 1099–1014, Oct 1963.

L. Bald, M. Spiess, R. Gruehn, and T. Kohlmann, “Beiträge zum thermischen Verhalten von Sulfaten. VI. Zum chemischen Transport von CuSO$_4$, Cu$_2$SO$_4$ und CuO,” *Zeitschrift für anorganische und allgemeine Chemie*, vol. 498, pp. 153–160, Mar. 1983.

M. Belaïche, M. Drillon, J. Aride, A. Boukharis, T. Biaz, and P. Legoll, “Application du modèle Heisenberg a la chaîne ferromagnétique d ions Cu(II) dans Cu$_2$SO$_4$,” *J Chim Phys*, vol. 1713–1719, 1991.

M. Drillon, M. Belaïche, and J. Heintz, “$G$. vilenueve”, a. boukharis” and j. aride,,” *Organic and Inorganic Low-Dimensional Crystalline Materials*, vol. 168, p. 421, 2013.

N. Takahashi, S. Okubo, H. Ohta, T. Sakurai, M. Fujisawa, and H. Kikuchi, “Dzyaloshinsky-Moriya Interaction Estimated by AFMR of Kagome Like Substance Cu$_3$O(SO$_4$)$_3$ Observed at 1.8K,” *Journal of Physics: Conference Series*, vol. 400, p. 032097, Dec. 2012.

T. Asai, H. Saheki, and K. Kiriyama, “Magnetic Studies on Basic Salts of Copper, Dicopper Arsenate Hydroxide, Dicopper Hydroxide Phosphate, and Dicopper Oxide Sulfate,” *Bulletin of the Chemical Society of Japan*, vol. 52, pp. 310–314, Feb. 1979.

P. R. Willmott, D. Meister, S. J. Leake, M. Lange, A. Bergamachi, M. Böge, M. Calvi, C. Cancelleri, N. Casati, A. Cervellino, Q. Chen, C. David, U. Flechsig, F. Gozzo, B. Henrich, S. Jäggi-Spielmann, B. Jakob, I. Kalichava, P. Karvinen, J. Krempl, A. Lüdeke, R. Lüscher, S. Maag, C. Quitmann, M. L. Ricci, M. Steinke, M. S. Streun, I. Vartiainen, M. Vitins, X. Wang, and R. Wüllschleger, “The Materials Science beamline upgrade at the Swiss Light Source,” *Journal of Synchrotron Radiation*, vol. 20, pp. 667–682, Sep 2013.
39. K. Momma and F. Izumi, “VESTA3 for three-dimensional visualization of crystal, volumetric and morphology data,” *Journal of Applied Crystallography*, vol. 44, pp. 1272–1276, Dec 2011.

40. L. Yang, M. Jeong, P. Babkevich, V. M. Katukuri, B. Náfrádi, N. E. Shaik, A. Magrez, H. Berger, J. Schefer, E. Ressouche, M. Kriener, I. Živković, O. V. Yazyev, L. Forró, and H. M. Rønnow, “J 1 - J 2 square lattice antiferromagnetism in the orbitally quenched insulator MoOPO 4,” *Physical Review B*, vol. 96, July 2017.

41. H. Papi, V. Y. Favre, H. Ahmadvand, M. Alaei, M. Khondabi, D. Sheptyakov, L. Keller, P. Kameli, I. Živković, and H. M. Rønnow, “Magnetic and structural properties of Ni-substituted magnetoelectric Co4Nb2O9,” *Phys. Rev. B*, vol. 100, p. 134408, Oct 2019.

42. P. Bag, P. R. Baral, and R. Nath, “Cluster spin-glass behavior and memory effect in Cr 0.5 Fe 0.5 Ga,” *Physical Review B*, vol. 98, Oct. 2018.

43. S. Pakhira, C. Mazumdar, R. Ranganathan, S. Giri, and M. Avdeev, “Large magnetic cooling power involving frustrated antiferromagnetic spin-glass state in R 2 NiSi 3 ( R = Gd , Er ),” *Physical Review B*, vol. 94, Sept. 2016.

44. D. W. Rogers, *Einstein’s “Other” Theory: The Planck-Bose-Einstein Theory of Heat Capacity*. Princeton University Press, 2005.

45. J. Rodríguez-Carvajal, “Recent advances in magnetic structure determination by neutron powder diffraction,” *Physica B: Condensed Matter*, vol. 192, no. 1, pp. 55 – 69, 1993.

46. C. Ritter, “Neutrons Not Entitled to Retire at the Age of 60: More than Ever Needed to Reveal Magnetic Structures,” in *Solid Compounds of Transition Elements*, vol. 170 of *Solid State Phenomena*, pp. 263–269, Trans Tech Publications Ltd, 3 2011.

47. J. Rodriguez-Carvajal, “BASIREPS: a program for calculating irreducible representations of space groups and basis functions for axial and polar vector properties, Part of the FullProf Suite of programs available at: www.ill.eu/sites/fullprof/,”

48. N. Takahashi, S. Okubo, H. Ohta, T. Sakurai, M. Fujisawa, and H. Kikuchi, “Dzyaloshinsky-Moriya Interaction Estimated by AFMR of Kagome Like Substance Cu2O(SO4) Observed at 1.8K,” *Journal of Physics Conference Series*, vol. 400, pp. 2097–, 12 2012.

49. I. Rousochatzakis, S. R. Mannana, A. M. Läuchli, B. Normand, and F. Mila, “Dzyaloshinskii-Moriya anisotropy and nonmagnetic impurities in the $s = \frac{1}{2}$ kagome system ZnCu$_3$(OH)$_6$Cl$_2$,” *Phys. Rev. B*, vol. 79, p. 214415, Jun 2009.

50. O. Cépas, C. M. Fong, P. W. Leung, and C. Lhuillier, “Quantum phase transition induced by Dzyaloshinskii-Moriya interactions in the kagome antiferromagnet,” *Phys. Rev. B*, vol. 78, p. 140405, Oct 2008.

51. H. M. Rønnow, “Structure and magnetic order of the diamond-kagome planar compound cu2oso4,” *STFC ISIS facility*, 2018.

52. H. M. Rønnow, “Magnetic order of the diamond-kagomé planar compound cu2oso4,” *Institut Laue-Langevin (ILL): Grenoble*, 2018.