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Toward Perfection: Kapellasite, $Cu_3Zn(OH)_6Cl_2$, a New Model $S = 1/2$ Kagome Antiferromagnet

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While much is becoming known experimentally about the effects of frustration in the classical limit, such as in the 3-dimensional pyrochlores[1−3] and 2-dimensional (2D) kagome lattice,[4−8] what happens in the $S = 1/2$ quantum limit is little characterized because of the scarcity of model materials. This has led to one of the most enduring problems in condensed matter physics: the search for the "resonating valence bond" (RVB) state. The state was proposed by Anderson more than two decades ago to underpin the transition to BCS superconductivity.[9] The RVB is a quantum state made by the spin pairing of electrons on different sites. Its highly entangled nature makes it an essential reference for the physical sciences, and for the current efforts in the development of states that can be exploited for quantum computing[10]

The $S = 1/2$ kagome antiferromagnet (KAFM) is a good candidate for the realization of the RVB state[11−13] and much excitement has been generated since the recent proposal of Herbertsmithite (also known as Zn−paratacamite) as a model $S = 1/2$ KAFM.[14] The material, named after the mineralogist Herbert Smith, is a doped member of the atacamite family in which one-quarter of the sites of a pyrochlore-like lattice are occupied by diamagnetic Zn^{2+}: the remaining sites are occupied by the Cu^{2+} spins to form the kagome net. Although it was initially hailed as a "perfect KAFM", NMR studies have shown that there is appreciable disorder in the Cu/Zn partitioning[15] and that the Dzyaloshinski−-Moriya (DM) interactions allowed in the kagome geometry play an important role.[16,17] Any intersite Cu/Zn substitution in Herbertsmithite is particularly significant as it introduces coupling between the kagome planes that destroys the

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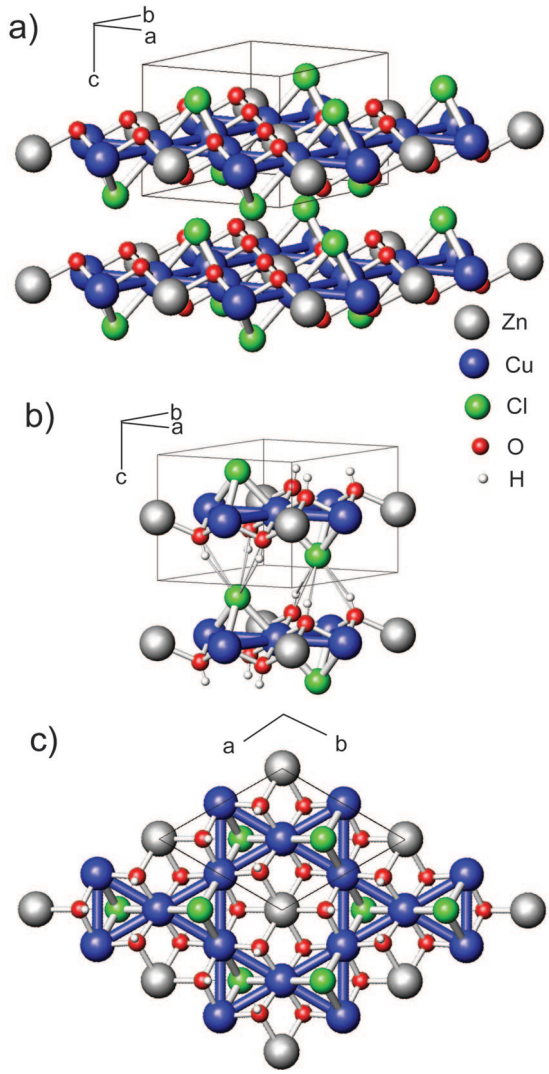

Figure 1. Quasi-2-dimensional lamellar structure of Kapellasite (a) without and (b) with the weak interplane O—H—Cl hydrogen bonds; (c) structure of Kapellasite projected down the [001] axis and the kagome lattice made from segregation of the Cu^{2+} and Zn^{2+} ions. The nearest neighbor Cu—Cu distances in the kagome plane and between kagome layers in Kapellasite are 3.15 and 5.73 Å, respectively.

2-dimensionality of the magnetic lattice. The local structure would then resemble the Cu_4 end-member clinoatacamite, γ-$Cu_2(OH)_3Cl$.[18−21]

In this paper, we report the synthesis and preliminary magnetic characterization of the newly discovered mineral Kapellasite, a metastable polymorph of Herbertsmithite, which shares its chemical formula, $Cu_3Zn(OH)_6Cl_2$.[22] Kapellasite is synthesized using a modified method to that used by Feitknecht from $ZnCl_2$ solution and copper metal acording to the following reaction:[23,24]

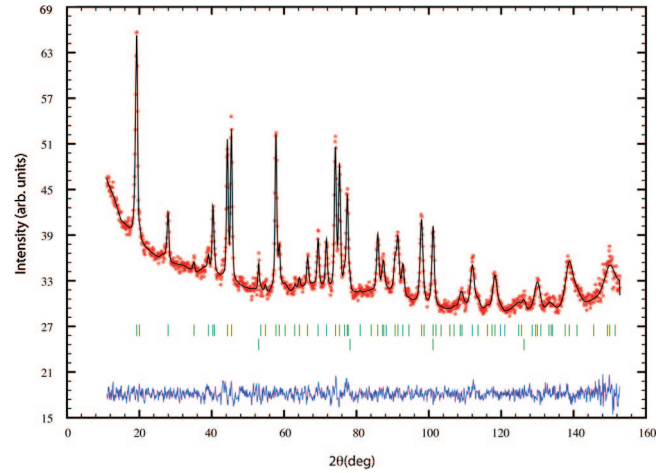

Figure 2. Fit to the powder neutron diffraction spectrum of Kapellasite, $Cu_3Zn(OH)_6Cl_2$, collected at room temperature over a period of 22 h using neutrons of wavelength 1.909 Å. The tick marks indicate the predicted locations of the nuclear scattering. The crosses correspond to the observed scattering, the line to the calculated diffraction pattern of the nuclear phase and the difference is shown below. The final goodness-of-fit parameter is $\chi^2 = 0.99$.

$$3Cu(s) + ZnCl_2(aq) + 6H_2O \rightarrow Cu_3Zn(OH)_6Cl_2(s) + 3H_2(g)$$

The crystal structure is a much better approximation to the KAFM with the 2D layers being only weakly coupled by O—H—Cl hydrogen bonds, giving rise to well defined cleavage planes along (001). The diamagnetic Zn^{2+} acts to dilute what would otherwise be a triangular net of Cu^{2+} to form a well defined kagome lattice (Figure 1). Whereas Cu/Zn disorder in Herbertsmithite introduces local exchange between the kagome planes, the perturbative effect in Kapellasite is expected to be much smaller due to the quasi-2D nature of the structure. Further, the exotic properties relating to the RVB state of the KAFM are expected to survive doping: the doped KAFM is a model for the CuO_2 planes in the underdoped cuprate superconductors.[25] This quantum behavior under the influence of disorder is quite different to that seen on the classical KAFMs where disorder can lead to Néel order.[26−28]

Powder neutron diffraction (PND) taken with the D1a diffractometer at the ILL from a 0.3 g sample of protonated Kapellasite showed that under these synthetic conditions, only a single copper hydroxychloride phase is formed, and the presence of unreacted copper particles was not observable. Rietveld refinement of the PND data using FullProf[29] showed the structure to be in good agreement with that

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(24) Copper powder (635 mg,10 mmol) was refluxed in a 0.25 M aqueous solution of $ZnCl_2$ (100 mL) for 1 h with oxygen bubbling before a blue precipitate (Kapellasite) had formed. The precipitate was then collected by hot filtration under a vacuum and washed with distilled water (3 × 20 mL), acetone and distilled water (3 × 20 mL), and finally acetone. A suspension of the collected product in distilled water (50 mL) was sonicated (5 min) before allowing the unreacted copper to settle to the bottom (5 min). The top 30 mL of suspension was then collected and diluted and the process was repeated. The top 30 mL of solution was then collected and the precipitate was collected from solution by centrifugation. The collected Kapellasite (190 mg, 13% yield) was then dried over silica gel for 24 h.
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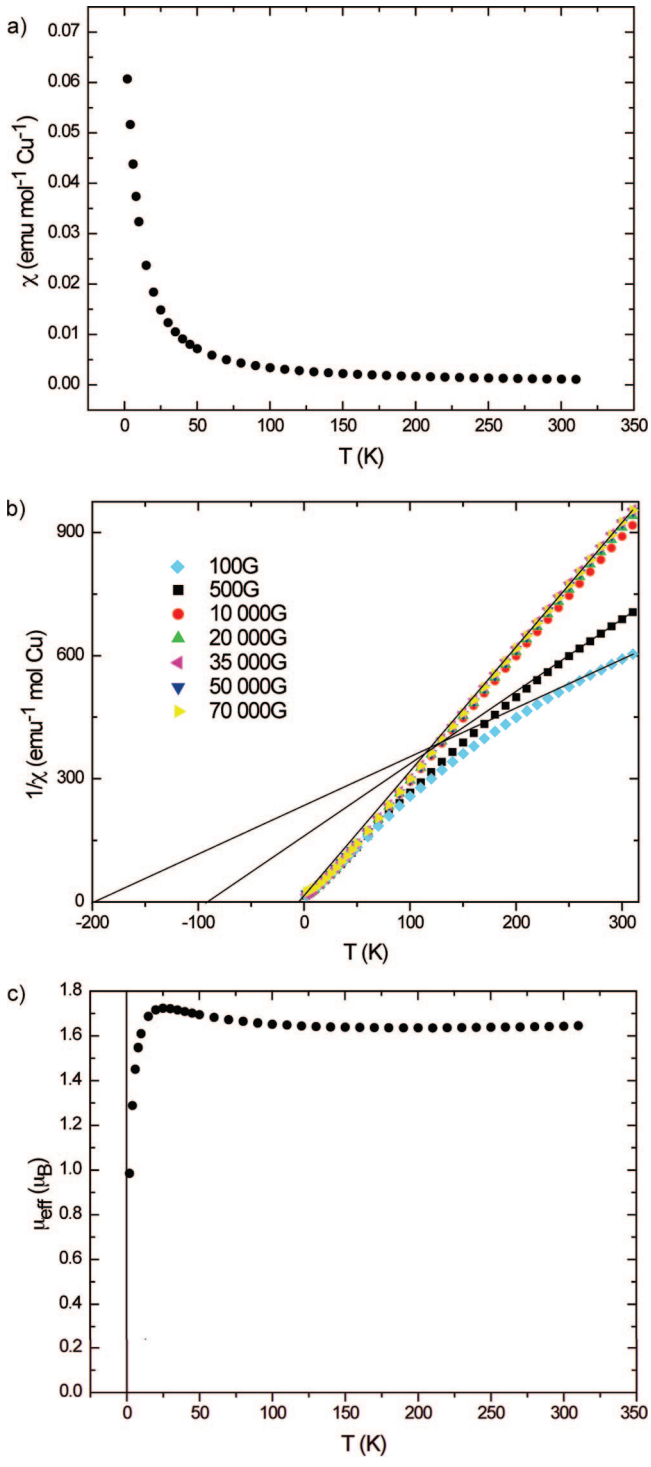

Figure 3. Dc magnetic susceptibility data for Kapellasite collected with a SQUID magnetometer. (a) Zero-field-cooled (○) and field-cooled (●) susceptibility taken in a measuring field of 10 000 G. (b) Inverse susceptibility measured in a variety of fields: in low magnetic fields a strong deviation from the Curie−Weiss law is seen above 200 K; this deviation lessens when the measuring field is increased. The straight lines are guides to the eye for Curie−Weiss-type behavior in 100, 500, and 70 000 G. (c) Effective moment, $\mu_{eff} = \sqrt{(8\chi T)}$, $S = 1/2$ moments beginning to condense into a nonmagnetic singlet state.

determined previously (Figure 2).[22] The crystal structure is expressed in space group $P\bar{3}m1$ and the refined crystallographic parameters are given in the Supporting Information, Table 1. There was no evidence of an intersite substitution, either of the Zn/Cu or Cl/OH within that quality of our data and all occupancies were left at their ideal values. A high degree of segregation is expected from the very different local geometries of the two metal sites. As in Herbertsmithite, the Jahn−Teller distorted Cu^{2+} resides more favorably on the tetragonally elongated 3f site; the Zn is effectively segregated at the 1b position and coordinated by a trigonally compressed octahedron of 6 equidistant Zn−O bonds. Bond balance calculations using VaList[30] are in good agreement with expected values: the bond valence sums and bond angles are shown in the Supporting Information, Tables 2 and 3, respectively.

The zero-field-cooled (ZFC) and field-cooled (FC) magnetic susceptibility measured in fields between 50 and 70 000 G do not indicate any clear antiferromagnetic transition down to $T = 2$K. Data collected in 1T are shown in Figure 3. The negative intercept of the inverse susceptibility with the temperature axis is found to decrease in magnitude with increasing measuring field. This behavior indicates that the field is coupling to a triplet component in the Hamiltonian of Kapellasite, which makes it hard to estimate a value of the Curie−Weiss temperature. In all fields, the temperature-dependence of the effective moment displays a marked reduction upon cooling below $T \approx 25$ K associated with a gradual moment collapse. Such behavior is not observed in the polymorph Herbertsmithite, and suggests that at low temperature the magnetic spins of Kapellasite condense into a nonmagnetic singlet state. The gradual change in its magnetic responses with temperature and the absence of any apparent ordering trasition down to 2 K suggests that the quantum spins in Kapellasite are condensing into a spin liquid state with gapless excitations. The field-dependence observed in the inverse susceptibility may then be explained by a DM-induced triplet component in this excitation manifold.

Further data, ideally collected with a local probe such as NMR or MuSR, is required to confirm whether the low temperature ground-state of this KAFM is indeed the nonmagnetic quantum state of the RVB model.

In conclusion, we present the crystal structure and preliminary magnetic susceptibility data from the new $S = 1/2$ kagome antiferromagnet Kapellasite, $Cu_3Zn(OH)_6Cl_2$. The kagome layers are only weakly coupled by O−H−Cl hydrogen bonds leading to highly 2D magnetic system. In contrast to its polymorph Herbertsmithite, Kapellasite displays a collapse in the effective moment on cooling below $T \approx 25$ K, suggesting that the spins of this quantum-frustrated magnet are condensing into a singlet ground state with gapless excitations.

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Supporting Information Available: Tables of crystallographic parameters, selected bond lengths, and selected bond angles (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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