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A Structurally Perfect $S = {}^1/_2$ Kagomé Antiferromagnet

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Nearly two decades ago, Anderson proposed that the resonating valence bond (RVB) state may explain the scatterless hole transport encountered in doped rare-earth cuprates.[1] The quantum spin liquid phase responsible for RVB is most likely to be found in low-dimensional, low-spin, and geometrically frustrated systems.[2] Accordingly, most theoretical investigations of RVB have concentrated on $S = {}^1/_2$ antiferromagnets in kagomé (corner-sharing triangular) lattices due to the higher degree of geometric frustration.[3] Materials featuring such lattices are predicted to display no long-range magnetic order due to competing antiferromagnetic interactions between nearest-neighbor spin centers. Though long sought, "no perfect $S = {}^1/_2$ Kagomé antiferromagnet has been up to now synthesized",[4] and accordingly, most theoretical predictions of such a lattice remain untested. Herein, we report the synthesis and preliminary magnetic properties of a rare, phase-pure, copper hydroxide chloride mineral featuring structurally perfect $S = {}^1/_2$ kagomé layers separated by diamagnetic Zn(II) cations.

We have employed a redox-based hydrothermal protocol to prepare pure, single-crystal jarosite-based materials ($AM_3(OH)_6(SO_4)_2$, A = alkali metal ion, M = V, Cr, Fe).[5] These compounds feature kagomé lattices composed of $M_3(OH)_6$ triangles; when M = Fe(III), spins are antiferromagnetically coupled and frustrated.[6] Substitution of the magnetic ion of Fe(III) ($S = {}^5/_2$) by Cu(II) ($S = {}^1/_2$) was attempted, but charge imbalance on the kagomé layers appears to prevent the preparation of a Cu(II) jarosite. We therefore turned our attention to developing hydrothermal methods for the preparation of the topologically similar kagomé series composed of Cu(II) ions—the atacamites—of general formula $MCu_3(OH)_6Cl_2$ (M = Co, Ni, Cu, Zn).[7] Our initial attempts to prepare these rare minerals in pure form began with the treatment of malachite ($Cu_2(OH)_2CO_3$) with NaCl and HBF_4 under hydrothermal conditions to form a blue microcrystalline compound whose powder X-ray diffraction pattern is consistent with that of the mineral claringbullite (PDF 86−0899),[8] where Cu(II) ions occupy the interlayer M site of $MCu_3(OH)_6Cl_2$. Further hydrothermal treatment of this solid with a large excess of $ZnCl_2$ afforded a green powder interdispersed with triangular plate crystals of $MCu_3(OH)_6Cl_2$ possessing a mixed M-site occupancy of Zn^{2+} and Cu^{2+}.

It is known that a solid solution exists for naturally occurring $Zn_xCu_{4-x}(OH)_6Cl_2$ specimens, such that even macroscopically "single" crystals may exhibit variable Cu/Zn composition at the interlayer site.[7] For $x < 0.33$, the crystal symmetry is monoclinic, resulting in a distorted kagomé lattice. At $x = 0.33$, the crystal symmetry increases to rhombohedral, and the Cu triangular plaquettes become equilateral. This high symmetry phase of intermediate Zn occupancy ($0.33 \leq x < 1$) is known as Zn−paratacamite (**1**).[10] The compositional end members are known as clinoatacamite[9] ($x = 0$) and herbertsmithite (**2**) ($x = 1$).[10]

The single-crystal X-ray structure of the compound with 33% Zn occupancy is shown in Figure 1. Details of the structure solution and refinement are provided in the Supporting Information. Two geometrically distinct metal sites are found. On the first site, a Cu(II) ion is surrounded by four equatorial hydroxide ligands and two distant axial chloride ligands. The hydroxide ligands bridge copper centers to form a kagomé lattice composed of $\{Cu_3(OH)_6\}$ triangles. On the other site, a Zn(II) ion is ligated by six hydroxide ligands in a trigonally compressed octahedral geometry. This site serves to link the kagomé layers into a dense three-dimensional structure. Although it is difficult to differentiate Cu and Zn by standard X-ray analysis, the two sites' distinct coordination environments suggest that the Jahn−Teller distorted Cu(II) ion should rest on the tetragonally elongated intralayer site, whereas the d^{10} Zn(II) ion should reside on the higher symmetry interlayer site. In support of this contention, several refinements of the structure were carried out in which either Zn or a Cu/Zn mixture was included on the intralayer site; all resulted in a significant increase in refinement residuals. Thus, Zn occupancy on the intralayer site is not reasonable. Upon refinement of the interlayer site, however, it was found that there was a slight but statistically significant preference[11] for a Cu/Zn mixture rather than Zn alone, such that Zn site occupancy refined to 33%. Best refinements of other crystals harvested from batch reactions show that Zn occupancy varies from crystal to crystal. These results highlight the difficulty of using X-ray diffraction to determine Zn/Cu composition. All materials used in these studies were therefore subject to chemical analysis to ascertain the Zn/Cu stoichiometry.

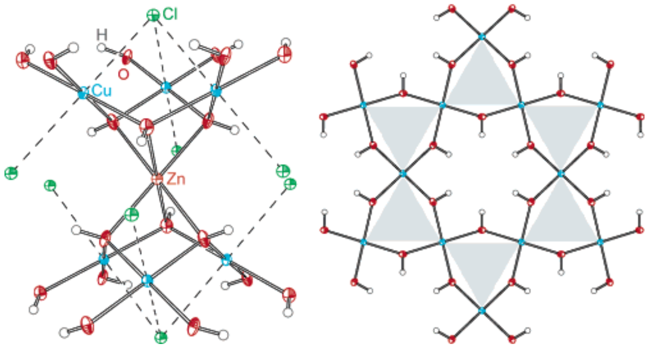

Figure 1. Crystal structure of Zn−paratacamite (**1**), $Zn_{0.33}Cu_{3.67}(OH)_6Cl_2$. Left: local coordination environment of intralayer $Cu_3(OH)_3$ triangles and interlayer Zn^{2+}/Cu^{2+} ion; the projection is parallel to the crystallographic *c* axis. Right: the $\{Cu_3(OH)_6\}$ kagomé lattice, projected perpendicular to the *c* axis. The pure Zn^{2+}-substituted compound **2** is isostructural to **1**. Selected interatomic distances (Å) and angles (deg) for **2**: Zn−O, 2.101(5); Cu−O, 1.982(2); Cu−Cl, 2.7698(17); Zn···Cu, 3.05967(16); O−Zn−O, 76.21(18), 103.79(18), 180.00(19); O−Cu−O, 81.7(3), 98.3(3), 180.0; O−Cu−Cl, 82.31(11), 97.68(11); Cl−Cu−Cl, 180.0; Cu−O−Cu, 119.1(2); Cu−O−Zn, 97.04(15).

The presence of Cu(II) ions in intra- and interlayer sites contributes to the overall magnetic susceptibility. To unravel the magnetic contributions of Cu(II) in the different sites, a series of

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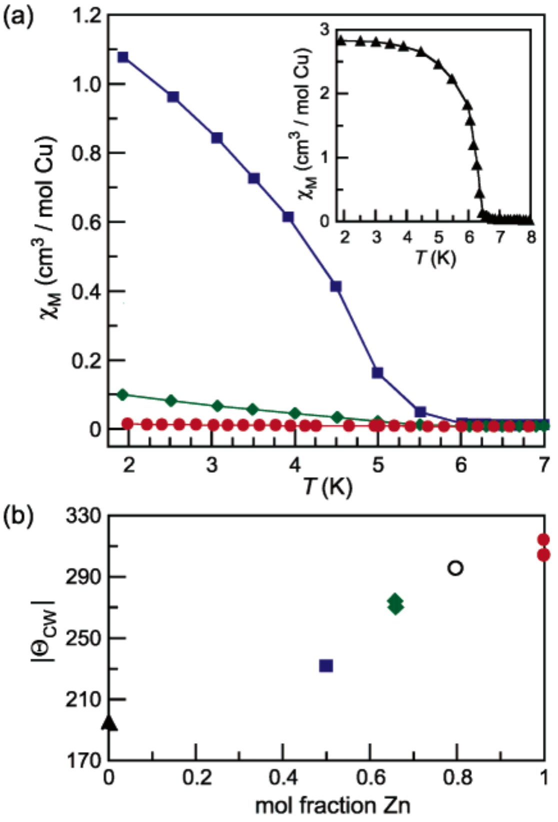

Figure 2. (a) Low temperature dependence of χ_M for compounds in the solid solution $Zn_xCu_{4-x}(OH)_6Cl_2$ for $x = 0$ (▲), 0.50 (blue, ■), 0.66 (green, ◆), and 1.00 (red, ●) as measured under ZFC conditions at 100 Oe (inset, $x = 0$). Lines shown to guide the eye. (b) Dependence of $|\Theta_{CW}|$ on interlayer Zn site occupancy; the additional point is for $x = 0.80$ (○).

Zn−paratacamites were prepared by hydrothermal synthesis according to the following:

$$3Cu_2(OH)_2CO_3 + 2MCl_2 + 3H_2O \rightarrow 2M\{Cu_3(OH)_6\}Cl_2 + 3CO_2 \quad (1)$$

where M = Cu and/or Zn. By varying the Cu/Zn stoichiometry, microcrystalline samples of the entire $0 \le x \le 1$ series can be prepared, with the end members ($x = 0$) and ($x = 1$) formed by the exclusive use of $MCl_2 = CuCl_2$ and $ZnCl_2$, respectively. Full experimental details are provided in the Supporting Information.

As Figure 2a shows, the magnetic susceptibility of **2** is distinct from that of its Cu-substituted congeners. $Cu[Cu_3(OH)_6Cl_2]$ shows a ferromagnetic transition with a critical temperature, $T_C = 6.5$ K. As Zn(II) ions are substituted onto the interlayer site, a ferromagnetic transition is maintained, but T_C decreases. At full Zn(II) occupancy, no magnetic ordering is observed for **2**. Fits of the high temperature inverse susceptibility data to the Curie−Weiss law yield large negative Θ_{CW} values (see Figures S3 and S4, Supporting Information), which are indicative of an antiferromagnetic exchange interaction for nearest-neighbor moments. As shown in Figure 2b, $|\Theta_{CW}|$ increases monotonically as more Zn is incorporated into the interlayer site; the strongest nearest-neighbor antiferromagnetic coupling is observed for **2** ($\Theta_{CW} = -314$ K).

The observed magnetism of the $MCu_3(OH)_6Cl_2$ series may be understood by a Goodenough−Kanamori analysis[12] of a Cu−O−Cu superexchange pathway. Within the kagomé layers, a $\angle Cu_{intra}-O-Cu_{intra} = 119.1°$ is expected to give rise to strong antiferromagnetic exchange,[13] as observed for all compounds. The absence of an ordering temperature in **2** is a clear indication of strong spin frustration, which inhibits the tendency for spins to order and hence suppresses T_C relative to Θ_{CW}. For **2**, spin frustration is sufficiently pronounced that no ordering is observed to the temperature limit of the SQUID susceptometer, despite the value of $\Theta_{CW} = -314$ K! With the introduction of Cu(II) ions into the interlayer site, a ferromagnetic exchange interaction is engendered owing to the introduction of an additional $Cu_{intra}-O-Cu_{inter}$ superexchange pathway; a $\angle Cu_{intra}-O-Cu_{intra} = 97.0°$ is expected to give rise to a weak ferromagnetic exchange interaction.[13] With spin frustration suppressing antiferromagnetic ordering within the kagomé layers, the ferromagnetic ordering event involving the interlayer Cu(II) ions is readily observed (see Figure 2a). Moreover, the increase in $|\Theta_{CW}|$ as the paramagnetic occupancy of the interlayer site decreases (Figure 2b) is consistent with the contribution of the ferromagnetic exchange interaction becoming less prevalent as $x \rightarrow 1$.

Ramirez has provided a measure for spin frustration by defining $f = |\Theta_{CW}|/T_C$, with values of $f > 10$ signifying a strong effect.[2] As is evident from $f > 157$, the pure phase of $ZnCu_3(OH)_6Cl_2$ (**2**) is one of the most frustrated spin systems discovered to date. Of consequence to RVB, this spin frustration occurs in a layered kagomé $S = {}^1/_2$ spin system. The foregoing results show that this long-sought spin lattice is achieved when the interstitial sites of kagomé layers composed of $Cu_3(OH)_6$ triangles are solely occupied by diamagnetic Zn(II) ions. Characterization of $Zn[Cu_3(OH)_6Cl_2]$ by neutron scattering is underway.

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Supporting Information Available: Synthetic protocol and magnetic characterization of $Zn_xCu_{4-x}(OH)_6Cl_2$ ($0 \le x \le 1$); crystallographic tables for $Zn_xCu_{4-x}(OH)_6Cl_2$ ($x = 0.33$, 0.42, 1.00) (pdf). Full X-ray crystallographic information, in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

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