A Cu$^{2+}(S = \frac{1}{2})$ Kagomé Antiferromagnet: Mg$_x$Cu$_{4-x}$(OH)$_6$Cl$_2$

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Received January 30, 2010; E-mail: nocera@mit.edu

Geometric frustration of magnetic ordering in triangle-based lattices is thought to be one avenue for inducing macroscopic quantum states in electron systems. Because of the triangular arrangement of ions, it is impossible to satisfy all of the nearest-neighbor interactions simultaneously (Figure 1a). This “frustration” suppresses classical magnetic long-range order (LRO) and is thought to be capable of producing novel quantum states such as the resonating-valence-bond (RVB) or “spin-liquid” ground state for a two-dimensional (2D) $S = \frac{1}{2}$ antiferromagnet. However, “structurally perfect” frustrated materials are rare; frequently, triangular lattices undergo a structural distortion at low temperature that relieves the magnetic frustration and gives rise to a classical ground state. One of the few known examples is the $x = 1$ end member of the paratacamite series Zn$_{x}$Cu$_{4-x}$(OH)$_6$Cl$_2$. It has a perfect 2D kagomé (corner-sharing triangle) lattice of Cu$^{2+}(S = \frac{1}{2})$ ions in Jahn–Teller-distorted O$_6$Cl$_2$ octahedra separated by layers of Zn$^{2+}$ in O$_6$ octahedra. However, the chemical similarity between Zn$^{2+}$ and Cu$^{2+}$ combined with the difficulty in differentiating Zn and Cu by X-ray and neutron diffraction techniques has complicated studies of this material, as site mixing of Zn and Cu in the kagomé planes may also account for the observed behaviors.

Herein we report the structural and magnetic characterization of a new series of compounds, Mg$_x$Cu$_{4-x}$(OH)$_6$Cl$_2$, that are isostructural with paratacamite. Whereas both Mg and Cu can occupy the interplane O$_6$ site, the ligand-field chemistry of non-Jahn–Teller-active Mg strongly disfavors its residency within the tetragonally distorted O$_6$Cl$_2$ coordination sites in the kagomé plane. This disparity in the ligand-field chemistry of Mg and Cu ensures minimal substitution of Cu by Mg into the kagomé interlayer.

Synthesis of Mg$_x$Cu$_{4-x}$(OH)$_6$Cl$_2$ proceeded in a manner analogous to that for paratacamite. In a typical reaction, Cu$_2$(OH)$_4$CO$_3$ and a large excess of MgCl$_2·6$H$_2$O (2–4 Mg per 1 Cu) were combined at 130–190 °C under hydrothermal conditions. After 2–3 days, a blue-green powder of Mg$_x$Cu$_{4-x}$(OH)$_6$Cl$_2$ was grown under interlayer MgO$_6$ octahedra separated by interlayer Mg$^{2+}$ atoms. The dashed line corresponds to the 95% confidence level for one extra parameter in the Hamilton R-ratio test. The lines are guides to the eye.

The c axis. These layers are built from corner-sharing CuO$_4$ plaquettes, which are tilted with respect to each layer. Triangles of the networks are bridged by MgO$_6$ octahedra between the layers separated by Cl$^{-}$ anions. Nominally, the in-plane, Jahn–Teller-distorted O$_6$Cl$_2$ sites are entirely occupied by Cu$^{2+}$, with Mg$^{2+}$ being incorporated solely into the interplane O$_6$ site, and thus, the formula can logically be written as (Mg$_x$Cu$_{4-x}$)(OH)$_6$Cl$_2$. To quantify the maximum amount of Mg at in-plane sites, several different tests were performed using the single-crystal data. First, refinements were performed assuming no mixing of Mg into the kagomé planes. Subsequently, the Mg/Cu ratio in the plane was allowed to vary, adding one additional parameter to the refinement. By the Hamilton R-ratio test, including this one extra parameter was barely on the edge of statistical significance at the 95% confidence level (1.008, 1.008, and 1.008 for 4, 5, and 6, respectively, versus a cutoff of 1.008). Furthermore, the freely refined Mg content in the kagomé planes was small in each case, at most 5.3 standard deviations away from zero [0.005(13), 0.032(9), and 0.047(9) for 4, 5, and 6, respectively]. Thus, the amount of mixing, if any, was small. As a more robust quantification of the maximum amount of Mg at the in-plane sites, Figure 1c shows values of the X-ray refinement statistic R1 obtained from refinements of the single-crystal X-ray data for 4, 5, and 6 at 100 K at various fixed levels of Mg in the kagomé layers (normalized to the value obtained with no mixing). In each case, the minimum is sharp and consistent with at most

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were collected for samples which exist only where interlayer coupling is present. Consequently, Cu$_2$+ This model also explains why the temperature at which the upturn due to significant disorder within the 2D kagome` planes.

in Mg$_{4}$ is 0.75, only a faint upturn remained. The suppression of ordering with increasing $x$ can be explained if the ferromagnetic-like behavior arises from magnetic coupling between the kagomé layer Cu$^+$ and the interlayer Cu$^+$ ions. When $x$ is small, there is significant coupling between neighboring kagomé layers, giving rise to regions of magnetic order, as is observed in the $x = 0$ end member, clinoatacamite. As the number of interlayer Cu$^+$ ions decreases (with increasing $x$), the interactions between in-plane and interplane sites due to Cu$^+$ in the O$_6$ octahedra are ferromagnetic and give rise to the magnetic order observed. These data also suggest that as $x$ approaches unity, no magnetic transition should remain, despite only a small maximum amount of Mg/Cu site disorder. The absence of magnetic disorder, which is similar to that observed in Zn$_{Cu}$ (OH)$_6$Cl$_2$ is consistent with an exotic ground state in these materials. Interlayer Cu$^+$ atoms in Mg$_{4}$ (OH)$_6$Cl$_2$ exhibit ferromagnetic coupling to in-plane, kagomé Cu$^+$ ions. However, magnetic ordering is suppressed when Cu$^+$ ions are absent from the interlayer. Within the kagomé layers, minimal substitution of Mg$^+$ for Cu$^+$ (±3%) is observed because of the significantly different ligand-field chemistry of these two ions. The absence of magnetic order and minimal site disorder within the kagomé planes suggests an unconventional magnetic ground state for Mg$_{4}$ (OH)$_6$Cl$_2$. These results imply that the lack of a magnetic-ordering transition in materials with this structure type, such as Zn$_{Cu}$ (OH)$_6$Cl$_2$, which also does not become magnetically ordered even at temperatures as low as 50 mK, is not due to chemical disorder but is indeed a result of the high spin frustration within the kagomé planes.

Acknowledgment. This work was supported by the MRSEC Program of the NSF under Award DMR-0819762 and the DOE grant DE-FG02-04ER46134. The authors acknowledge helpful discussions with Oleg Tchernyshyov, Yiwen Chu, and Patrick Lee.

Supporting Information Available: Complete synthetic protocols, Curie–Weiss fits of magnetic susceptibilities, and X-ray diffraction results (CIF). This material is available free of charge via the Internet at http://pubs.acs.org.

References

(12) The mineral haydite has a similar formula, Mg$_4$(OH)$_6$Cl$_2$, but a different structure than the compounds reported here.

JA1008322