Barlowite as a canted antiferromagnet: Theory and experiment

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We investigate the structural, electronic, and magnetic properties of the newly synthesized mineral barlowite Cu4(OH)6FBr which contains Cu2+ ions in a perfect kagome arrangement. In contrast to the spin-liquid candidate herbertsmithite [ZnCu3(OH)6Cl2], kagome layers in barlowite are perfectly aligned due to the different bonding environments adopted by F− and Br− compared to Cl−. With the synthesis of this material we unveil a design strategy for layered kagome systems with possible exotic magnetic states. Density functional theory calculations and effective model considerations for Cu4(OH)6FBr, which has a Cu2+ site coupling the kagome layers, predict a three-dimensional network of exchange couplings, which together with a substantial Dzyaloshinskii-Moriya coupling lead to canted antiferromagnetic ordering of this compound in excellent agreement with magnetic susceptibility measurements on single crystals yielding \( T_N = 15 \) K.

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Since the successful synthesis of herbertsmithite \([\text{ZnCu}_3(\text{OH})_6\text{Cl}_2]\) [1], spin-liquid candidates based on spin-1/2 kagome lattices have been intensively investigated in recent years [2,3]. The paratacamite family of compounds has proven to be a fertile ground for kagome materials with different properties. The Zn, Cu\(_{\text{III}}\)-(OD)\(_6\)Cl\(_2\) series of materials has been found to form valence-bond solids due to distortions of the kagome layer in monoclinic space groups [4]. The replacement of Zn\(^{2+}\) in ZnCu\(_3\)(OH)\(_6\)Cl\(_2\) by a nonmagnetic ion, such as Mg\(^{2+}\), possibly leads to another spin-liquid candidate [5] as does the replacement of 2Cl\(^{−}\) by SO\(_2\)\(^{2−}\) [6]. On the other hand, magnetic ions between the kagome layers lead to compounds that order magnetically [7]. Although realizations of quantum spin liquids have been desperately searched for [8], so far, together with the triangular-lattice molecule-based organic materials [9,10], herbertsmithite has been considered one of the best candidates [11]. However, ZnCu\(_3\)(OH)\(_6\)Cl\(_2\) has not been free from controversy as Zn\(^{2+}\) and Cu\(^{2+}\) are similar in size, and both kagome layers diluted with nonmagnetic Zn\(^{2+}\) [3] as well as magnetic Cu\(^{2+}\) ions replacing Zn\(^{2+}\) between the kagome layers [12] are possible. Therefore, it would be desirable to devise a crystal modification of herbertsmithite that would make the Cu\(^{2+}\) and Zn\(^{2+}\) sites less similar in order to increase the tendency of Cu\(^{2+}\) ions to form the kagome layer as well as the tendency of the nonmagnetic transition-metal ion to stay away from the kagome plane. Recently [13] one of the authors introduced the mineral barlowite Cu\(_4\)(OH)\(_6\)FBr as a layered structure of two-dimensional (2D) Cu-based perfect kagome planes and reported the observation of antiferromagnetic order at low temperatures based on thermodynamic measurements on polycrystalline samples. In the present paper we go beyond previous studies and suggest a synthetic route to successfully obtain perfect kagome structures, exemplarily realized in the mineral barlowite. Such structures offer an important alternative to herbertsmithite. They are chemically and physically flexible enough so that via doping or application of pressure one can explore not only potential quantum spin-liquid behavior at half-filling, but also other exotic states, such as flat bands at certain fillings inducing Nagaoka ferromagnetism [14] or the presence of Dirac points at 4/3 filling that could lead to unusual symmetry-protected metals or superconductors [15].

Furthermore, we resolve the microscopic origin of the electronic and magnetic behaviors of barlowite, which has a Cu\(^{2+}\) site coupling the kagome layers. Via a combination of density functional theory (DFT) calculations and magnetic susceptibility measurements we find this material to be a canted antiferromagnet below \( T < T_N \) with a canting angle away from the kagome plane of 4.5°.

In herbertsmithite, the Cl− binding environment is partially covalent, partially hydrogen bonded, as shown in Fig. 1(a). This leads to a horizontal staggering of kagome layers [Fig. 1(b)] as Cu\(^{2+}\) triangles can be placed either above or below a Cl− ion but not both above and below. We suggest using a mixed halide system where the strong hydrogen bond acceptance of the F− ion is used to create a hydrogen-rich pocket with six hydroxyl ions; on the other hand, Br− can form six covalent bonds to three Cu\(^{2+}\) ions above and three below [Fig. 1(c)]. Following this recipe via the chemical synthesis of Cu\(_4\)(OH)\(_6\)Br\(_3\), we arrive at perfectly aligned kagome planes as shown in Fig. 1(d). This compound is known as the mineral barlowite [16].

Single crystals of barlowite Cu\(_4\)(OH)\(_6\)FBr were grown synthetically through the hydrothermal reaction of copper carbonate basic (malachite), with perbromic acid in the presence of ammonium fluoride. The crystal structure of Cu\(_4\)(OH)\(_6\)FBr was determined by single-crystal x-ray diffraction measurements [17] at ambient temperature and is shown in Fig. 2. Barlowite crystallizes in \( P\text{6}3\text{mmc} \) symmetry with each intralayer Cu\(^{2+}\) [Cu(1)] ion lying on a site of \( 2/m \) symmetry (see Table I). This intralayer Cu\(^{2+}\) exhibits a strongly tetragonally distorted octahedral coordination with four equatorial Cu-0 bonds of 1.954(1) Å and two axial Cu-Br bonds of 3.022 Å. Interlayer Cu\(^{2+}\) [Cu(2)] sites lie on a general position and are thus 1/3 occupied and disordered over three equivalent positions.

In order to characterize barlowite electronically and magnetically, we combined first-principles DFT calculations with...
FIG. 1. (Color online) Chloride environment of (a) herbertsmithite compared to bromide and fluoride environments of (c) barlowite. (b) A mix of covalent and hydrogen bonding in ZnCu$_3$(OH)$_6$Cl$_2$ leads to three kagome layers shifted with respect to each other as shown by differently colored Cu$_{2}^{2+}$ sites. (d) Preference of Br$^-$ for covalent bonding and of F$^-$ for hydrogen bonding leads to perfect alignment of kagome layers in Cu$_4$(OH)$_6$FBr [only Cu(1) sites are shown here].

near the Fermi level is of Cu 3d orbitals hybridized with O 2p orbitals. The band structure along the high-symmetry path Γ’-M-K-Γ reflects the dispersion of the kagome layers [dominated by Cu(1) d states] whereas the band structure along the high-symmetry path A-L-H-A at $k_z = 0.5$ arises from the 2D lattice formed by the interkagome Cu(2) atoms. The electronic structure of the kagome layer resembles that of the spin-liquid compound herbertsmithite very well [21]. However, both herbertsmithite and barlowite are Mott insulators. In order to reflect this behavior in the band-structure calculations we show in Fig. 3(c) the density of states calculated with the GGA + $U$ functional with $U = 6$ eV.

The exchange couplings we obtain from total energy calculations are listed in Table II. The nearest-neighbor coupling

FIG. 2. (Color online) Crystal structure of Cu$_4$(OH)$_6$FBr ($P6_3/mmc$ space group, No. 194). Note that the Cu(2) site with Wyckoff position 12j is $\frac{1}{4}$ filled.
TABLE II. Exchange-coupling constants for Cu$_4$(OH)$_6$FBr, calculated with GGA + $U$ at $U = 6$ eV, $J_0 = 1$ eV and with atomic-limit double-counting correction. Positive (negative) $J$ values denote antiferromagnetic (ferromagnetic) couplings.

<table>
<thead>
<tr>
<th>Name</th>
<th>$d_{CuCu}$ (Å)</th>
<th>Type</th>
<th>$J_i$ (K)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Kagome layer coupling</td>
<td></td>
</tr>
<tr>
<td>$J_1$</td>
<td>3.3399</td>
<td>Cu(1)-Cu(1)</td>
<td>177</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Interlayer couplings</td>
<td></td>
</tr>
<tr>
<td>$J_2$</td>
<td>2.7632</td>
<td>Cu(1)-Cu(2)</td>
<td>-205</td>
</tr>
<tr>
<td>$J_3$</td>
<td>3.1885</td>
<td>Cu(1)-Cu(2)</td>
<td>-32</td>
</tr>
<tr>
<td>$J_4$</td>
<td>4.6532</td>
<td>Cu(1)-Cu(1)</td>
<td>5</td>
</tr>
<tr>
<td>$J_6$</td>
<td>5.5264</td>
<td>Cu(2)-Cu(2)</td>
<td>16</td>
</tr>
</tbody>
</table>

in the kagome plane is $J_3 = 177$ K for barlowite. This is very similar to the value $J = 182$ K obtained for herbertsmithite, reflecting the fact that Cu-O-Cu angles are very similar in both compounds (117° in barlowite and 119° in herbertsmithite). The fact that barlowite has Cu$^{2+}$ ions at interlayer positions [Cu(2)] determines the magnetic behavior of this system at low temperatures. Specifically, we find that ferromagnetic interlayer couplings ($J_1 = -205$ and $J_2 = -32$ K) exist between Cu(1) (in the kagome layer) and Cu(2) (interlayer). Further exchange paths become increasingly and significantly weaker—comparable or smaller than 0.1 J. Within the Cm unit cell chosen here, it was not possible to separate the coupling $J_5$ corresponding to a Cu(1)-Cu(2) distance of 5.2359 Å from the small ferromagnetic $J_2$. The vertical coupling $J_4$ between the kagome planes is negligibly small. The resulting Heisenberg Hamiltonian parameters are illustrated in Fig. 4. Note that due to the lowering of the symmetry from $P6_3/mmc$ to $Cmcm$ for the calculations, the path of the ferromagnetic one-dimensional Cu(2) chains has become uniquely defined. In reality, these chains wiggle through the crystal according to the actual positions of Cu(2), which is randomly chosen from the three possible sites. We estimate an error bar on the Heisenberg Hamiltonian parameters on the order of 20% and possibly larger for the smaller couplings because the calculated values depend strongly on the essentially unknown size of the Hubbard parameter $U$ and because of the tendency of DFT to overestimate the stability of the ferromagnetic state.

The magnetic properties of barlowite were measured using a commercial Quantum Design superconducting quantum interference device (SQUID) magnetometer in the temperature range of 2 K $\leq$ $T$ $\leq$ 300 K on a single crystal of mass $m = 3.4$ mg. The susceptibility measurements were performed in various fields up to 1 T with orientation parallel and perpendicular to the hexagonal $c$ axis. For the latter orientation the magnetization was measured in fields up to $\pm$5 T. The experimental data have been corrected for the temperature-independent diamagnetic core contribution of the constituents [23] and the magnetic contribution of the sample holder.

By considering the exchange parameters obtained from DFT, we calculated $1/\chi_{mol}$ using tenth-order high-temperature series expansion [24]. The result is shown in Fig. 5 together with the experimental $1/\chi_{mol}$ data for $B \parallel c$. We find that a very good fit of the experimental observations, shown by the solid line, is obtained with $J_3 = 177$ K and $J_1 = -0.94J_3$, $J_2 = -0.16J_3$, and $J_6 = 0.15J_3$ in combination with a $g$ value of 2.20. Given the strongly distorted octahedral Cu$^{2+}$ environment, implying anisotropic $g$ values ranging from 0.1 $\leq$ $\Delta g/g$ $\leq$ 0.15 [25,26], a $g$ value of 2.2 for $B \parallel c$ is reasonable. The so-derived values of the exchange couplings are within the error bars of the DFT calculation confirming that the DFT analysis of barlowite is reliable.

The inset of Fig. 5 exhibits the $\chi_{mol}T$ curve as a function of temperature for $T \approx 100$ K in fields $B = 0.1$ T for $B \parallel c$ and $B \perp c$ both after ZFC. At 300 K (not shown) $\chi_{mol}T$ is about 0.367, a value slightly smaller than the one for isolated spin-1/2 ions. With decreasing temperature $\chi_{mol}T$ becomes continuously reduced down to approximately 0.261 around 20 K. Such a large $\chi_{mol}T$ value in an antiferromagnetically coupled system at a temperature of $T \lesssim J_3/10$ is only possible when in addition a ferromagnetic coupling exists which is

FIG. 4. (Color online) Important exchange paths of Cu$_4$(OH)$_6$FBr (see Table II). The notation $J_i, i$ = 1–6, denotes nearest through sixth nearest Cu-Cu neighbors.

FIG. 5. (Color online) Inverse molar susceptibility as a function of temperature (open circles) taken at $B = 0.1$ T for $B \parallel c$ together with a theoretical approximation to $1/\chi$ calculated by tenth-order high-temperature series expansion [24] (see the main text). Inset: $\chi_{mol}T/Cu^{2+}$ ion as a function of temperature in fields $B = 0.1$ T for $B \parallel c$ and $B \perp c$ both after cooling in zero field (ZFC). The broken line indicates the value for a spin $S = 1/2$ of 0.376.
of similar size. Upon cooling to below about 18 K, $\chi_{\text{mol}} T$ for both orientations starts to increase with a maximum slope around 15 K, followed by a pronounced maximum. The overall magnetic response, especially the steep increase in $\chi_{\text{mol}} T$ in the paramagnetic phase close to $T_N$, is a clear signature of a phase transition into long-range antiferromagnetic order characterized by canted spins exhibiting a small ferromagnetic component [27]. The maximum of $\chi_{\text{mol}} T$ for $B \parallel c$ exceeds that for $B \parallel c$ by more than a factor of 2. These temperature and orientation dependences indicate that the easy axes are tilted against the kagome plane.

Figure 6 exhibits the magnetization measured for $B \parallel c$ at 2 K. The blue open squares correspond to the virgin curve taken after cooling in zero field, and the red diamonds correspond to data taken upon subsequent field cycling. Lower right inset: blowup of the high-field section. Upper left inset: blowup of the low-field section.

Ref. [23] this value together with the saturation magnetization can be used to determine the tilt angle relative to the perfectly antiferromagnetically aligned spins resulting in a canting angle of approximately $4.5^\circ$. We assign the difference between this canting angle and the orientation of the basal plane of the Cu octahedra to the existence of a Dzyaloshinskii-Moriya (DM) interaction allowed by symmetry in barlowite, which acts here like an easy-plane anisotropy. The DM vector $D$ lies within the mirror plane [27], which in barlowite is perpendicular to the kagome plane. An estimate of the size of $|D|$ is given by $|D|/J_1 \simeq \Delta g/g = 0.1$, which is substantial. As worked out in detail in Ref. [28] the DM interaction in frustrated kagome systems can induce a long-range canted antiferromagnetic order. According to Ref. [28] we can conclude from our experimental findings that $D$ is definitely not perpendicular to the kagome plane. In contrast, it has a significant in-plane component $D_p$.

According to our calculations, cf. Table II, there are no ferromagnetic interactions between the interlayer Cu(2) ions larger than $0.1 J_1$, which rules out that the weak ferromagnetism originates from ordering among these interlayer spins. However, the interlayer spins influence the magnetization in the ordered state. There are strong ($J_1$) and moderate ($J_2$) ferromagnetic couplings between the spins on the kagome plane [Cu(1)] and the interlayer spins [Cu(2)]. As a result there are no degrees of freedom left for the Cu(2) spins in fields which are small compared to these couplings. The spins align parallel to the Cu(1) spins belonging to the kagome layers and are thus tilted against the kagome planes. They contribute to the remanent magnetization according to their relative abundance (25%).

To summarize, as exemplarily shown for barlowite, we propose a synthetic route for kagome-based structures with the possibility of interesting phases, such as ordered magnetic phases with different ordering vectors, spin liquid, Dirac metal, or even unconventional superconductivity. On one hand, substitutions at the interlayer cation site [15] may be effective for the realization of such states; on the other hand, the existence of the mineral clarinburgullite Cu$_4$(OH)$_2$FCl [29,30], which is isostructural to barlowite but has different combinations of anions—the Br$^-$ ion of barlowite is replaced by Cl$^-$—demonstrates that the synthesis route outlined here opens the path to a family of compounds. Finally, our combined first-principles calculations with susceptibility measurements identify the low-temperature behavior of barlowite as a canted antiferromagnet with a canting angle of approximately $4.5^\circ$.

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[17] CCDC 1019246 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.