Barlowite as a canted antiferromagnet: theory and experiment

Harald O. Jeschke,1 Francesc Salvat-Pujol,1 Elena Gati,2 Nguyen Hieu Hoang,2 Bernd Wolf,2 Michael Lang,2 John A. Schlueter,3 and Roser Valentí1

1 Institut für Theoretische Physik, Goethe-Universität Frankfurt, Max-von-Laue-Straße 1, 60438 Frankfurt am Main, Germany
2 Physikalisches Institut, Goethe-Universität Frankfurt, Max-von-Laue-Straße 1, 60438 Frankfurt am Main, Germany
3 Division of Materials Research, National Science Foundation, Arlington, Virginia 22230, USA

We investigate the structural, electronic and magnetic properties of the newly synthesized mineral barlowite Cu$_4$(OH)$_6$FBr which contains Cu$^{2+}$ ions in a perfect kagome arrangement. In contrast to the spin-liquid candidate herbertsmithite ZnCu$_3$(OH)$_6$Cl$_2$, kagome layers in barlowite are perfectly aligned due to the different bonding environments adopted by F$^-$ and Br$^-$ compared to Cl$^-$. We perform density functional theory calculations to obtain the Heisenberg Hamiltonian parameters of Cu$_4$(OH)$_6$FBr which has a Cu$^{2+}$ site coupling the kagome layers. The 3D network of exchange couplings together with a substantial Dzyaloshinskii-Moriya coupling lead to canted antiferromagnetic ordering of this compound at $T_N = 15$ K as observed by magnetic susceptibility measurements on single crystals.

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away from the kagome plane. The purpose of this work is
(1) to suggest such a strategy, exemplarily realized in the
mineral barlowite and (2) to unveil the microscopic origin
of the electronic and magnetic behavior of this system
via a combination of density functional theory calculations
and magnetic susceptibility measurements. Besides
the search for ideal quantum spin liquids, the electronic
structure of kagome materials offers a large variety of
interesting properties, like for instance the presence of flat
bands at certain fillings that induces Nagaoka ferromagnetism
[13] or the presence of Dirac points at 4/3 filling
that could lead to unusual symmetry protected metals or
superconductors [14].

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)\(_6\)FBr,
we arrive at perfectly aligned kagome planes as shown
in Fig. 1(d). This compound is known as the mineral
barlowite [15]. So far, only some of its properties have
been reported [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 struc-
ture of Cu\(_4\)(OH)\(_6\)FBr was determined by single crystal
X-ray diffraction measurements [17] at ambient temper-
arature and is shown in Fig. 2. Barlowite crystallizes in
P\(_{6}_3/mmc\) space group 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-O bonds
of 1.954(1) Å and two axial Cu-Br bonds of 3.022 Å. In-
terlayer Cu\(^{2+}\) (Cu(2)) sites lie on a general position and
are thus 1/3 occupied and disordered over three equiv-
alent positions.

### Table I. Structural parameters for Cu\(_4\)(OH)\(_6\)FBr at T = 298(2) K (P\(_{6}_3/mmc\) space group, a = 6.799(4) Å, c = 9.3063(13) Å, Z = 2).

| Atom  | Site | x    | y    | z    | U (Å\(^2\)) | Occ. |
|-------|------|------|------|------|-------------|------|
| Cu(1) | 6g   | 0.5000 | 0   | 0    | 0.01540(17) | 1    |
| Cu(2) | 12j  | 0.62884(12) | 0.2577(2) | 1/4 | 0.0133(4)  | 1/4  |
| O     | 12k  | 0.79768(18) | 0.20232(18) | 0.0916(2) | 0.0137(4) | 1    |
| H     | 12h  | 0.852(3)   | 0.148(3) | 0.127(4) | 0.021     | 1    |
| Br    | 2c   | 1/3     | 1/3  | 1/4  | 0.0184(2)  | 1    |
| F     | 2b   | 0       | 0    | 1/4  | 0.0238(10) | 1    |

In order to characterize barlowite electronically and
magnetically, we combined first principles density func-
tional theory (DFT) calculations with susceptibility mea-
surements. Our DFT calculations were performed on the
basis of the full-potential non-orthogonal local-orbital basis
(FPLO [18], employing the generalized gradient approx-
imation (GGA) [19] as well as GGA+U [20] functionals. The Hubbard parameter U was set to 6 eV,
the Hund’s rule coupling J\(_H\) to 1 eV. The exchange-
coupling constants between spin-1/2 Cu\(^{2+}\) ions were ob-
tained by mapping GGA+U total energy differences of
several Cu\(^{2+}\) spin configurations onto a spin-1/2 Heisen-
berg model [21, 22]. In order to make a sufficient number
of Cu\(^{2+}\) sites inequivalent to allow for various spin con-
figurations, the symmetry was lowered from the C\(_{mcn}\)
to the C\(_m\) space group (No. 8) containing 6 inequivalent
Cu\(^{2+}\) positions.

In Fig. 3(a)-(b) we show first the GGA band structure
and density of states of barlowite. The main contribution
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 lay-
ers (dominated by Cu(1) d states) while the band struc-
ture along the high-symmetry path A-L-H-A at k\(_z\) = 0.5
arises from the 2D lattice formed by the inter-kagome

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**FIG. 3.** (a) GGA band structure and (b) GGA density of states (DOS) of Cu\(_4\)(OH)\(_6\)FBr. DOS is given in states per eV and formula unit. High symmetry points M = (1/2, 0, 0), K = (1/3, 1/3, 0), A = (0, 0, 1/2), L = (1/4, 0, 1/2), H = (1/3, 1/3, 1/2) were chosen to reflect the P\(_{6}_3/mmc\) symmetry of the real material rather than the C\(_{mcn}\) symmetry used for computa-
tional purposes. (c) GGA+U density of states for U = 6 eV,
J\(_H\) = 1 eV and ferromagnetic order. Note that the size of the gap
is related to the value of U considered.
TABLE II. Exchange coupling constants for Cu$_4$(OH)$_6$FBr, calculated with GGA+U at $U = 6$ eV, $J_H = 1$ eV and with atomic-limit double-counting correction.

| Name          | $d_{Cu-Cu}$ (Å) | Type               | $J_i$ (K) |
|---------------|-----------------|--------------------|----------|
| Kagome layer coupling |                | Cu(1)-Cu(1)        | 177      |
| $J_3$         | 3.3390          |                    |          |
| Interlayer couplings |              |                    |          |
| $J_1$         | 2.7632          | Cu(1)-Cu(2)        | -205     |
| $J_2$         | 3.1885          | Cu(1)-Cu(2)        | -32      |
| $J_4$         | 4.6532          | Cu(1)-Cu(1)        | 5        |
| $J_6$         | 5.5264          | Cu(2)-Cu(2)        | 16       |

FIG. 4. Important exchange paths of Cu$_4$(OH)$_6$FBr. The notation $J_i$, $i = 1, 2, 3, \ldots$ denotes 1st, 2nd, 3rd, \ldots Cu-Cu neighbors. Positive (negative) $J$ values denote antiferromagnetic (ferromagnetic) couplings. Exchange constants were determined to be $J_3 = 177$ K (kagome layer), $J_1 = -205$ K and $J_2 = -32$ K. A coupling $J_6 = 16$ K connecting two Cu(2) sites along the red bond is indicated by a curved arrow. Note that disordered Cu(2) sites in the $P6_3/mmc$ space group lead to random permutations of the two weak and one strong ferromagnetic couplings between every Cu(1) triangle above and below a Cu(2) site. Larger couplings are shown with cylinders of larger diameter.

FIG. 5. Inverse molar susceptibility as a function of temperature (open circles) taken at $B = 0.1$ T for $B \parallel c$ together with Curie-Weiss fits (red broken lines) for 200 K $\leq T \leq 300$ K and 50 K $\leq T \leq 100$ K. Also shown is a theoretical approximation to $1/\chi$ calculated by 10th-order high-temperature series expansion [23], using the calculated value $J_3 = 177$ K and $J_1 = -0.94 J_3$, $J_2 = -0.16 J_3$ and $J_6 = 0.15 J_3$ as well as a $g$ factor of 2.20 (blue solid line). Note that $J_1$, $J_2$ and $J_6$ agree with the calculated values within their error bars. Inset: Effective magnetic moment per 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).

Cu(2) atoms. We observe that the electronic structure of the kagome layer resembles the electronic structure of the spin-liquid compound herbertsmithite very well [22]. 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 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, 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 ($J_1 = -205$ K 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 0.1J. Within the Cm unit cell chosen here, it was not possible to separate the coupling $J_3$ corresponding to a Cu(1)-Cu(2) distance of 5.2359 Å from the small ferromagnetic $J_2$. The vertical coupling $J_1$ 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 of 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 SQUID magnetometer in the temperature range 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 $B$ oriented in plane and along 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 \cite{26} and the magnetic contribution of the sample holder.

Figure 5 shows the inverse molar magnetic susceptibility (open circles) as a function of temperature for $B \parallel c$. The 1/$\chi_{\text{mol}}$ data can be approximated by a Curie-Weiss-like behavior (red broken lines in Fig. 5) at the upper and lower ends with an antiferromagnetic Weiss-temperature $\theta = (155 \pm 2)$ K for 200 K $\leq T \leq 300$ K and $(22 \pm 2)$ K for 50 K $\leq T \leq 100$ K. This behavior is consistent with the presence of two dominant magnetic coupling constants of different sign, suggested by our DFT calculation.

By considering the exchange parameters obtained from DFT, we calculated $1/\chi_{\text{mol}}$ using 10th-order high-temperature series expansion \cite{23}. We find that a very good fit of the experimental observations, shown by the solid blue line in Fig. 5, 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 $\leq \Delta g/g \leq 0.15$ \cite{24, 25}, a $g$ value of 2.2 for $B \parallel c$ is reasonable. The 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. 6 exhibits the effective magnetic moment $n_{\text{eff}}$ per Cu$^{2+}$ ion as a function of temperature for $T \leq 100$ K in fields $B = 0.1$ T for $B \parallel c$ and $B \perp c$ both after cooling in zero field (ZFC). At 300 K (not shown) $n_{\text{eff}}$ is about 1.69 $\mu_B$/Cu$^{2+}$, a value slightly smaller than the one for isolated spin-1/2 ions. With decreasing temperature $n_{\text{eff}}$ becomes continuously reduced down to approximately 1.2 $\mu_B$ around 20 K. Such a large effective moment in an antiferromagnetically coupled system at a temperature $T \lesssim J_3/10$ is only possible when in addition a ferromagnetic coupling exists which is of similar size. Upon cooling to below about 18 K, $n_{\text{eff}}$ for both orientations starts to increase with a maximum slope around 15 K. Upon further cooling, $n_{\text{eff}}$ passes over a maximum followed by a rapid decrease. This behavior is a clear signature of a phase transition into long-range antiferromagnetic order characterized by canted spins exhibiting a small ferromagnetic component. This is also corroborated by the observation of a hysteresis loop observed at 2 K and shown in Fig. 5. The maximum of $n_{\text{eff}}$ for the field aligned parallel to the hexagonal planes exceeds that for fields oriented perpendicular to the planes by nearly a factor of two, indicating that the easy axis of barlowite is oriented along the hexagonal plane.

Figure 5 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. This was possible after carefully compensating for finite remanent fields present in the superconducting magnet of the SQUID magnetometer. Also shown is the full hysteresis loop obtained upon cycling the field in the range $-5$ T $\leq B \leq +5$ T. The hysteresis loop closes at $|B| \geq 4$ T at 2 K, cf. lower right inset to Fig. 4. Upon field cycling (red symbols), following the virgin run, the magnetization exhibits a large slope for fields below 0.1 T. At this field level, $M$ reaches approximately 10% of the expected saturation magnetization of 1 $\mu_B$ per Cu$^{2+}$ ion. On further increasing the field $M(B)$ increases almost linearly and reaches a value of 0.23 $\mu_B$/Cu$^{2+}$ at 5 T, which is close to 1 $\mu_B$/f.u. The evolution of $M$ upon varying $B$ indicates a discontinuous magnetization process which has to be taken into account when analyzing magnetic data taken at fields below 4 T. The upper inset of Fig. 4 shows the low-field sector of the hysteresis loop. For $B = 0$ barlowite has a remanent magnetization of approximately 0.3 $\mu_B$ per formula unit. According to Ref. 26 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°. Such a moderate spin canting out of the hexagonal plane is consistent with the existence of a Dzyaloshinskii-Moriya (DM) interaction allowed by symmetry in barlowite. According to Ref. 27, the DM vector $D$ lies within the mirror plane which in barlowite is perpendicular to the kagome plane. An estimate of the size of $|D|$ is given by $|D|/J_3 \simeq \Delta g/g = 0.1$ which is substantial.

In summary, the structure of barlowite with perfectly aligned kagome layers opens a new 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. Our combined first principles calculations with susceptibility measurements identifies the low temperature behavior of barlowite as a canted antiferromagnet with a canting angle of approximately 4.5°.

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