Kagome quantum spin systems in the atacamite family

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We present the hydrothermal synthesis, as well as structural and chemical analysis of single crystals of the compounds EuCu 3+(OH) 6Cl 3, Zn x Cu 1−x (OH) 6(NO 3) 2 and haydeeite, MgCu 3(OH) 6Cl 2, all arising from the atacamite family. Magnetic and specific-heat measurements down to 1.8 K are carried out for these systems. EuCu 3(OH) 6Cl 2 has a frustrated antiferromagnetic Cu 2+ ground state with order at 15 K, a strong anisotropy and increased magnetization from Van Vleck paramagnetic Cu 2+ contributions. ZnCu 3(OH) 6(NO 3) 2 reveals antiferromagnetic order at 9 K and measurements on haydeeite single crystals confirm the ferromagnetic order at 4.2 K with the easy axis within the kagome plane. These results prove that the atacamite family presents a broad class of materials with interesting magnetic ground states.

I. INTRODUCTION

The discovery of the first reported prototype with magnetic Cu 2+ ions arranged on a kagome layer presenting a quantum spin liquid (QSL) 1 in herbertsmithite (ZnCu 3(OH) 6Cl 2), 2 triggered enormous interest for this novel ground state. The dominant Cu-O-Cu antiferromagnetic superexchange of J = −197 K 3 in the kagome plane is strongly frustrated due to the geometrical arrangement of the ions. Considering the possibility of variable Zn for Cu substitution in Zn x Cu 1−x (OH) 6Cl 2, one can influence the magnetic properties of the compounds: increasing the Zn in between these kagome layers leads to their magnetic decoupling and thus to a suppression of the magnetic order 4,5. For the composition ZnCu 3(OH) 6Cl 2 (x = 1), no magnetic long-range order is registered down to T = 50 mK 6. Later on, it has been realized that some Zn-Cu antiferromagnetic order (up to 15% in terms of occupation parameters) is always present in herbertsmithite 5,6, which has led to the search for further kagome materials, with less amount of structural disorder. The atacamite family of compounds presents a rich field of different substitution possibilities 7 based on the three basic polyhedral units of Cu 2+ (OH) 6Cl: atacamite, clinogatacamite and botallackite, allowing substitutions both on the Cu and Cl place. Cationic substitutions would dilute the concentration of Cu 2+ ions between and in the kagome planes, while those on the anionic sites would have a direct impact on the spatial separation of these active planes. Furthermore, it was proposed that substituting trivalent ions on the valent Zn/Cu ions will lead to a correlated Dirac-kagome metal combining Dirac electrons, strong interactions, and frustrated magnetism 8. However, experimentally it was found that the structure presents charge balancing with additional Cl − rather than electron doping, as seen for the nonmagnetic Y 2,10 and the magnetic Nd, Gd and Sm 11 ions.

In table 1 we present the whole class of M x Cu 1−x−x(OH) 6X 2, with detailed information on the structure type and magnetism. The atom type of substitution is highlighted by a color and its crystal ionic radius is given in the fourth column. The given space group in the fifth column enables a division into two main structural variants: the herbertsmithite R3m type structure containing ABC stacked kagome layers with intermediate layers of the substituent and the kapellase type with AA stacked layers, where the substituent is in the kagome layer in the center of the star (see figure 2). Other groups are the basic structures with possible substitutions on the halide site, then the crossover paratacamite over herbertsmithite to the substitutions of x = 2 leading with nonmagnetic ions to one dimensional chain systems and finally the x = 4 entirely substituted variants. The last type shows the structural variance of this family and the possibility of undescribed intermediate candidates. We want to highlight the work of reference 12 which already shows a rich amount of variants only for the M 2(OH) 3Cl,Br,I candidates. Besides the shown atacamite type a “kapellase-type” structure called α variant was found by Oswald and Feitknecht 12 for Co, Ni, Mg, Fe, Mn with x = 4 substitution. As well as paratacamite variants of Co/Fe and botallackite types for Br/I both for Cu, Co, Ni, Fe as well as Mn.

The columns (6-9) give details about the magnetic properties and is followed by some structural details of the Cu ions (10-12), where Cu K stands for the shortest copper distances in the kagome plane and Cu_inter for the distances between these layers ignoring Cu atoms in between. The column number 12 contains the bonding angle of Cu-O-Cu where the largest and thus dominating J is chosen. In the last two columns references are given. So far the only kagome systems of this family presenting no magnetic order down to mK temperatures are both ZnCu 3(OH) 6Cl 2 herbertsmithite and kapellase, ZnCu 3(OH) 6FBr called Zn-barlowite and MgCu 3(OH) 6Cl 2 tondiiite which all have a strong Zn-Cu or Mg-Cu exchange. Other quantum spin liquid candidates of the family are ones presenting isolated trimers found in SrCu(OH) 3Cl 13 and ZnCu 3(OH) 6SO 4 14, which so far only exist as polycrystals. In addition to these compounds we present another example of the P3m1 structure with a trivalent Eu 3+ ion realized in EuCu 3(OH) 6Cl 3. As well as an example of an antiferromagnetic system with no strong frustration effects, observed in ZnCu 3(OH) 6(NO 3) 2 and the successful single crystal growth of the ferromagnetic haydeeite MgCu 3(OH) 6Cl 2.
II. EXPERIMENTAL DETAIL

For the single crystal growth a hydrothermal Parr 4625 autoclave with a 575 ml filling capacity operated by a Parr 4842 power supply including a 982 Watlow controller was used.

The energy dispersive X-ray spectra (EDS) were recorded with an AMETEK EDAX Quanta 400 detector in a Zeiss DSM 940A scanning electron microscope (SEM). A layer of carbon was sputtered on the isolating single crystals using a Balzers Union FL-9496.

X-ray powder diffraction data were collected on a Bruker D8 Focus using a Cu X-ray generator and the Rietveld refinement of the X-ray data was done using the fullprof suite [47].

For the single crystal structure determination the data were collected at 173 K on a STOE IPDS II two-circle diffractometer with a Genix Microfocus tube with mirror optics using Mo Kα radiation (λ = 0.71073 Å). The data were scaled using the frame scaling procedure in the X-AREA program system [18].

The structure was solved by direct methods using the program SHELXS [49] and refined against F² with full-matrix least-squares techniques using the program SHELXL-97 [19]. The H atoms bonded to O were found in a difference map and was isotropically refined with the O-H distances restrained to 0.84(1) Å.

The specific-heat and magnetic measurements were collected with the standard options of a Physical Property Measurement System from Quantum Design in a temperature range of 1.8 to 350 K.

III. EuCu₃(OH)₆Cl₂

A. Synthesis

Single crystals of EuCu₃(OH)₆Cl₂ were prepared in the Parr autoclave with a temperature profile adapted from the optimised one for Y₃Cu₉(OH)₁₉Cl₈ [2]. For the crystallization, we prepared duran glass ampoules as follows: The ampoules were loaded with 0.6513 g CuO and 2 g EuCl₃·6H₂O, solved in 5 ml distilled water and then sealed at air. They were placed in the autoclave, which was filled with distilled water to ensure the same pressure as in the ampoules. The autoclave was heated up to 270°C in four hours and subsequently cooled down to 170°C with 1 K/h, followed by a fast cooling to room temperature. Afterwards, the ampoules were opened and the content was filtered with distilled water. The ampoules contained a few larger single crystals, some smaller ones and a pellet. The crystals have blue colour and a hexagonal shape with typical sizes up to 1 x 1 x 0.25 mm³ (see figure 2c). Similar to Y₃Cu₉(OH)₁₉Cl₈ [2] and haydeeite, the crystal habitus gives information about all crystallographic axes, with the a and b axis being the corners of the hexagon and the c axis perpendicular to the surface of the platelets. Attempts with lower and higher EuCl₃·6H₂O content in the solutions were also successful but lead to smaller single crystals. However, the Eu content does not change with varying salt amount, which was deduced from EDS.

Furthermore, a growth in an external temperature gradient similar to [50] led to large single crystals of up to 2 x 2 x 0.75 mm³ (shown in figure 2b). We used 2 g pre-reacted EuCu₃(OH)₆Cl₂ in a solution of 1 g EuCl₃·6H₂O with 5 ml H₂O sealed in a thick walled quartz ampoule of 15 cm length. Then we placed this ampoule into an external gradient of 2°C/cm, with 250°C at the hot end and 220°C at the cold end. After several weeks the whole powder was recrystallized.

B. EDS Analysis

We measured EDS in the SEM on several crystals of different batches both of polished and untreated single crystals. In figure 1 an EDS spectra is shown with the SEM image on the inset showing a clean surface with no impurity phases. The resulting at% are given in the figure and are in overall agreement with stoichiometric values of EuCu₃(OH)₆Cl₂. We measured several points on many crystals of different batches and did not observe any variance regarding the Eu-Cu ratio.

This is typical for the P-3n1 structure, which has no intermediate substitutions and no paratacamite like crossover structure. E.g. kapellasite and haydeeite [? ? ] stabilizes a certain substitution amount above one. By directly comparing only the Cu/Eu ratio we found the Eu amount, assuming Eu₄Cu₉₋ₓ(OH)₆Clₓ, to be not increased with an average of x_Eu = 1.01 ± 0.01.

![FIG. 1. EDS analysis on a polished single crystal of EuCu₃(OH)₆Cl₂. In a table the measured at% are given compared to the stoichiometric values, not including the H atoms. The inset shows a SEM image, which would have shown impurity phases as grey-scaled contrast, proving the homogeneity of the crystal.](image-url)
| Type name | Mineral name | Formula | $r_{\text{crys}}$ [pm] | $t_{\text{crys}}$ | Point group | Magnetic lattice | Magnetic order | $\Theta_W$ [K] | f | Cu$_K$ [Å] | Cu$_\text{inter}$ [Å] | $\angle$(Cu1-O1-Cu1) | Reference | sc growth |
|-----------|--------------|---------|----------------|--------------|-------------|---------------|----------------|----------------|---|------------|----------------|----------------|-------------|-----------|
| parent:  | atacamite   | Cu$_2$(OH)$_2$Cl | 72 | Pnma | P | 9 | -125 | 14 | 3.432 | 5.464 | 124.39 | [18] | - |
| clinoatacamite | Cu$_2$(OH)$_2$Cl | 72 | P2$_1$/n | P | 6.5 | -200 | 30 | 3.410 | 5.023 | 120.21 | [18] | - |
| botallackite | (Ni/Co/Fe/Mn/Cu)$_2$-Cl$_3$(Cl/Br/I) | 69/ 74.5/ 75/ 83 | P2$_1$/m | T | 7.2/10/14 | 0.41 | 0 | 3.059 | 5.716 | 107.91 | [12, 18] | - |
| brochantite | Cu$_4$(OH)$_6$SO$_4$ | 258 | P2$_1$/n | ‘1D’ | 6.3 | -90 | 14 | 3.005 | 5.062 | 124.5 | [21] | - |
| rouante | Cu$_2$(OH)$_2$(NO$_3$)$_3$ | 179 | P2$_1$ | T | 11 | -12 | 1 | 3.05 | 6.929 | 110.33 | [22, 23] | - |
| claringbullite | Cu$_4$(OH)$_6$Cl$_2$ | 126 | P6$_3$/mmc | P | 17 | -33 | 2 | 3.337 | 2.737 | 117.56 | [22, 22] | - |
| barlowite | Cu$_4$(OH)$_6$Br$_2$ | 188, 126 | P6$_3$/mmc | P | 15 | -136 | 9 | 3.339 | 2.757 | 117.21 | [23] | - |
| paratacamite | Zn$_2$Cu$_{4-x}$-x(OH)$_6$Cl$_2$ | 73 | R3m | K | 6 | -231 | 38.5 | 3.416 | 3.110 | 122.28 | [4, 28] | x = 0.5/0.25 |
| - | G$_{60}$,Cu$_{3x}$-x(OH)$_6$Cl$_2$ | 62 | R3m | K | 5 | -256 | 55 | 3.421 | 5.066 | 118.88 | [20] | - |
| - | Zn$_2$Cu$_3$(OH)$_6$Cl$_2$ | 72 | R3m | K | - | -300 | $\infty$ | 3.416 | 5.054 | 119.05 | [32] | - |
| - | Zn$_2$Cu$_3$(OH)$_6$Br$_2$ | 73 | R3m | K | - | -300 | $\infty$ | 3.416 | 5.087 | 118.92 | [32, 23] | - |
| - | Cu$_4$(OH)$_6$Cl$_2$ | 74.5 | R3m | K | 3 | -40 | 13 | 3.421 | 5.096 | 119.19 | [32, 32] | - |
| - | Cu$_4$(OH)$_6$Cl$_2$ | 95 | P2$_1$/n | K | - | -150 | 75 | 3.015 | 5.758 | 108.50 | [32] | - |
| haydeeite | Mg$_2$Cu$_3$(OH)$_6$Cl$_2$ | 72 | P3m1 | K | 4.3 (FM) | 28 | 7 | 3.137 | 5.750 | 104.98 | [31, 35] | this paper |
| kapellasite | Zn$_2$Cu$_3$(OH)$_6$Cl$_2$ | 73 | P3m1 | K | - | 9.5 | $\infty$ | 3.150 | 5.733 | 105.84 | [57, 39] | - |
| - | Zn$_2$Cu$_3$(OH)$_6$(NO$_3$)$_2$ | 73, 179 | P2$_1$ | K | 7.5 | 0 | 0 | 3.065 | 6.927 | 104.07 | this paper | this paper |
| misakiite | Mn$_2$Cu$_3$(OH)$_6$Cl$_2$ | 83 | P$3m1$ | T | 10 | -25 | 3 | 3.208 | 5.710 | 108.00 | [20] | - |
| - | Y$_2$Cu$_3$(OH)$_6$Cl$_3$ | 90 | P3m1 | K | 12 | -100 | 8.33 | 3.250 | 5.618 | 117.36 | [10] | - |
| - | Cu$_2$(OH)$_6$Cl$_3$ | 90 | R3 | K | 2.2 | -100 | 45 | 3.250 | 5.679 | 117.47 | [10] | - |
| - | Cu$_2$(OH)$_6$Cl$_3$ | 94.7 | P3m1 | K | 15 | -400 | 119.3 | 3.418 | 5.630 | 119.34 | this paper | this paper |
| - | Sm$_2$Cu$_3$(OH)$_6$Cl$_3$ | 95.8 | P3m1 | T | 18 | -106 | 5 | 3.432 | 5.659 | 120.1 | [10] | - |
| - | Nd$_2$Cu$_3$(OH)$_6$Cl$_3$ | 98.3 | P3m1 | T | 20 | -345 | 19 | 3.411 | 5.625 | 119.30 | [14] | - |
| centennialite | Cu$_3$Cu$_2$(OH)$_6$Cl$_2$ | 100 | P3m1 | K | 5 | -56 | 11 | 3.324 | 5.760 | 114.09 | [32] | - |
| ▼ | Cu$_2$(OH)$_2$Cl | 73 | P2$_1$/m | 1D | ? | ? | ? | 3.195 | 5.688 | 107.70 | [44] | - |
| ▼ | Zn$_2$Cu(OH)$_2$Cl | 83 | P$2_1$/m | 1D | 29 | -80 | 3 | 3.302 | 5.791 | 114.12 | [20] | - |
| ▼ | SrCu(OH)$_2$Cl | 117 | Pmm2$_1$ | Trimer | -135 | $\infty$ | 3.395 | 6.972 | 119.40 | [13] | - |
| ▼ | Zn$_2$Cu$_3$(OH)$_6$SO$_4$ | 73.258 | P2$_1$/a | Trimer | -79 | $\infty$ | 2.781 | 4.441 | 91.86 | [14] | - |

TABLE I. List of the atacamite family divided into four classes of structures each sorted by the size of the substitution ions. The table includes the mineral name if naturally existing, the chemical formula, the 6 fold coordinated radius of the substituted ion, the structural space group, the lattice type of the magnetic ion (K: kagome, P: pyrochlore, T: triangular and 1D: chains), the magnetic transition temperature, the Curie-Weiss temperature with the resulting frustration as well as the Cu arrangements. Column 10-12 describe the structure with first the relevant magnetic ion distance, then the distance between the sought kagome layers (ignoring the position in between) and finally the highest Cu-O-Cu bonding angle. In the next-to-last column first the reference for the magnetic properties is given, then the one of the structure and in the last column a reference for single crystal growth. If the substitution ion itself is magnetic the whole line is written in italic.
EuCu$_3$(OH)$_6$Cl$_3$ crystallizes in the kapellasite type structure P-3m1 with an additional Cl position just like Y, Nd, Sm and Gd [9–11]. The structure was obtained by single crystal diffraction and confirmed with powder diffraction. It is a general Van Vleck part (see Ref. [55]) and the Curie-Weiss contribution. We fitted the experimental data in the full range from 1.8 K to 350 K at a high field of 9 T in figure 3. In this temperature regime Eu$^{3+}$ ions cause pronounced Van Vleck paramagnetism, which gives a separate magnetic contribution in addition to the magnetism from the Cu$^{2+}$. The susceptibility in this temperature range reveals a pronounced anisotropy, $\chi_{\parallel}/\chi_{\perp}$ from 1.7 at 350 K to 2.5 at 50 K plotted in the inset of figure 3. This anisotropy is most likely attributed to the Van Vleck contribution, similar as it was observed in Ref. [53, 54]. There, the anisotropy arises from a splitting of the $^1$F$_1$ level due to a crystal electric field. In literature this anisotropy was analyzed for a tetragonal symmetry of the Eu$^{4+}$, while in EuCu$_3$(OH)$_6$Cl$_3$ the europium atoms are located on a site with hexagonal symmetry. We fitted the experimental data in the full range from 1.8 K to 350 K at a high field of 9 T in figure 3 with the sum of a general Van Vleck part (see Ref. [72]) and the Curie-Weiss contribution from three Cu$^{2+}$ ions following the formula

$$\chi_{\text{mod}} = \frac{3 C}{T + \Theta_W} + \frac{N_A \mu_0 \mu_B^2}{3 \lambda} \left( \frac{24 + (13.5 - 1.5)e^{-\lambda/(k_B T)}}{1 + 3e^{-\lambda/(k_B T)}} + \ldots \right)$$

D. Magnetic susceptibility

In this section, we present a thorough magnetic analysis on EuCu$_3$(OH)$_6$Cl$_3$ single crystals. To obtain larger masses for a reduced noise ratio, four single crystals were aligned with either the magnetic field parallel (\parallel) or perpendicular (\perp) to the kagome plane. We start with the analysis of the susceptibility at 9 T for temperatures between 2 and 350 K, shown in figure 3. The susceptibility data at 9 T with the field aligned (black dots) and perpendicular to the kagome plane (red dots). The line is obtained by a fit using both Van Vleck and Curie-Weiss contribution. On the inset the temperature dependant anisotropy of perpendicular/parallel susceptibility is shown.

C. Structure

EuCu$_3$(OH)$_6$Cl$_3$ crystal viewed along the c-axis revealing the center of the star in the kagome plane typical for the kapellasite P-3m1 structure. a) Image of a large EuCu$_3$(OH)$_6$Cl$_3$ crystal with a coaligned twin obtained from an external gradient growth. b) Laue-Image and a picture of a large EuCu$_3$(OH)$_6$Cl$_3$ single crystals from a growth in the auto clave showing nice hexagonal shape.

FIG. 2. a) Image of the P-3m1 structure viewed onto the ab plane. There, the orange star like kagome arrangement of the Cu atoms is apparent. The pink europium atoms are positioned in the center of the star in the kagome plane directly revealing the EuCu$_3$(OH)$_6$Cl$_3$ crystal with a coaligned twin obtained from an external gradient growth. c) Image of two examplous untreated blue EuCu$_3$(OH)$_6$Cl$_3$ single crystals from a growth in the auto clave showing nice hexagonal shape.

| position | x/a | y/b | z/c | Occ. $U_{100}$ | Site Sym. |
|----------|-----|-----|-----|---------------|-----------|
| Eu1      | 0   | 0   | 0.5 | 1             | 0.0131(3) 1b -3m. |
| Cu1      | 0   | 0   | 0.5 | 1             | 0.0123(4) 3f   |
| Cl1      | 0.666667 | 0.333333 | 0.1359(4)   | 0.0190(6) 2d   |
| Cl2      | 0   | 0   | 0   | 1             | 0.0176(7) 1a   |
| O1       | 0.8066(4) | 0.1934(4) | 0.6318(7)   | 0.0122(8) 6i    |
| H1       | 0.790(8) | 0.210(8) | 0.776(4)    | -             |

TABLE II. Structural table obtained by refining single crystal diffraction data on EuCu$_3$(OH)$_6$Cl$_3$ single crystal measured at 173 K. A trigonal P-3m1 (#164) structure with a unit cell of $a = b = 6.8363(14)$ Å and $c = 5.6301(13)$ Å, $\alpha = \beta = 90^\circ$, $\gamma = 120^\circ$ was found, where the occupation was fixed to 1.
We present the low temperature behaviour of 
for a field of 0.50 Oe. It is necessary to accurately define the Eu\(^{3+}\) Van Vleck contributions. Assuming a generally similar behavior as for the tetragonal symmetry, we get a spin orbit value of roughly \(\lambda = (2\lambda_\parallel + \lambda_\perp)/3 = (2\cdot210 + 586)/3\) K \(\approx 335\) K comparable to \(\text{Eu}_2\text{CuO}_4\) with \(\lambda = 315\) cm\(^{-1}\) \(\approx 300\) K.\(^{53}\) The Curie-Weiss temperatures was calculated in this global fit yielding roughly \(\Theta_W \approx -400\) K.

From a \(\sqrt{xT}\) plot (not shown) the whole material reveals increased effective moment values of \(\mu_{\text{eff}}^{||} = 3.25\mu_B\) and \(\mu_{\text{eff}}^{\perp} = 2.5\mu_B\) at 350 K compared to the theoretical one for Cu\(^{2+}\) of 1.73 \(\mu_B\) as a result of the mixture with the Van Vleck contribution of Eu\(^{3+}\).

The transition temperatures can best be determined by the derivate of \(\chi\cdot T\) at a tiny field of 50 Oe.

In figure 4 we present the low temperature behaviour of the susceptibility data of \(\text{EuCu}_3(\text{OH})_6\text{Cl}_3\) field cooled at 0.1 T both measured with the field aligned (red) and perpendicular to the kagome plane (black). Inset: Derivative of \(\chi\cdot T\) at a tiny field of 50 Oe.

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure4.png}
\caption{The main figure shows the low temperature part of the susceptibility data of \(\text{EuCu}_3(\text{OH})_6\text{Cl}_3\) field cooled at 0.1 T both measured with the field aligned (red) and perpendicular to the kagome plane (black). Inset: Derivative of \(\chi\cdot T\) at a tiny field of 50 Oe.}
\end{figure}

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure5.png}
\caption{Excerpt of the M(H) curves measured at 2 K (black), 12 K (dark grey) and 20 K (light grey) with a field applied parallel to the kagome plane. The inset shows the full range for a measurement at 2 K for both parallel (black) and perpendicular fields (red).}
\end{figure}

A small but well defined hysteresis can be seen for magnetic field within the kagome plane. However, the spontaneous moment below \(T_{N_1}\) is only \(0.5\cdot10^{-3}\mu_B\) per Cu and \(1\cdot10^{-3}\mu_B\) below \(T_{N_2}\). This shows, that the magnetic order has a tiny in-plane ferromagnetic component. For fields perpendicular to the kagome layers nearly no hysteresis was observed. At higher magnetic fields, both directions present a linear \(M(H)\) dependence, with a higher slope for the direction perpendicular to the kagome plane. At 9 T, \(M\) reaches only about 0.05 and 0.14 \(\mu_B/Cu\) for the two field directions, which is well below the saturation magnetization of 1 \(\mu_B\) per Cu\(^{2+}\) ion. Furthermore, also the Van Vleck contribution from Eu might contribute to the magnetization at higher fields, but is difficult to entangle from the Cu magnetism. For that purpose a reference compound with Zn instead of Cu would be necessary, which however, is not known to exist so far.

E. Specific heat

The observed magnetic transitions in the magnetic measurements were also analyzed on several crystals by specific heat. This is essential to exclude contributions from small foreign phases to be the origin of the observed magnetic signals. We show a measurement between 1.8 K and 39 K on a single crystal of 8.61 mg. The general specific heat curve divided by temperature is shown in figure 5 for a field of 0 and 9 T. We roughly estimated this phonon part in a temperature range 20 - 32 K from a linear fit of C/T vs T\(^2\) plot. With \(\beta = 0.625(6)\) mJ/mol we get an estimated debye temperature of \(\Theta_D \approx 390\) K slightly above the one of \(\text{Y}_3\text{Cu}_9(\text{OH})_1\text{Cl}_8\)\(^{53}\). We notice that this estimate is very rough and only used to show an order of magnitude for the phon contribution. The


reason is apparent from figure[6] because also at 30 K a clear $T^3$ dependance of the specific heat is not obtained, due to magnetic contributions from the fluctuating moments, hindering a more accurate fit of the phonon contribution. At 15 K we observe a broad peak in the specific heat data, proving that the transition observed in the magnetic measurements is an intrinsic property of EuCu$_3$(OH)$_6$Cl$_3$. This transition shows no field dependance for fields up to 9 T. This is in line with the M(H) curve up to 9 T, where no saturation was reached, showing that the field scale of 9 T is far below the energy scale of the dominant magnetic coupling. The entropy connected with the small peak is well below the full ordered moment of Cu, in agreement with the large frustration coefficient found in the magnetic measurements.

**IV. Zn$_x$Cu$_{4-x}$(OH)$_6$(NO$_3$)$_2$**

**A. Synthesis**

Powder samples of ZnCu(OH)$_6$(NO$_3$)$_2$ were prepared by a solid state reaction of 0.337 g ZnO with 1 g Cu(NO$_3$)$_2$ $·$ 6 H$_2$O and 0.6585 g CuO sealed in a Parr 4749 acid digestion vessel heated to 220°C for two days then rapidly cooled to room temperature.

Single crystals of Zn$_x$Cu$_{4-x}$(OH)$_6$(NO$_3$)$_2$ were prepared in the Parr autoclave with a temperature profile adapted from the optimised one from Y$_3$Cu$_9$(OH)$_{19}$Cl$_8$. For the crystallization, we placed duran glass ampoules filled with the solution in the autoclave and filled it with distilled water to ensure the same pressure as in the ampoules. The ampoules were loaded with 0.4 g CuO and 2-4 g Zn(NO$_3$)$_2$ $·$ 6 H$_2$O (see table III) solved in 3 ml distilled water and then sealed at air. The autoclave was heated up to 270°C in four hours and subsequently cooled down to 140°C with 1.4 K/h, followed by a fast cooling to room temperature. Afterwards, the ampoules were opened and the content was filtered with distilled water. The ampoules contained a few larger single crystals, some smaller ones and a pellet. The crystals have blue colour and a square shape with typical sizes up to 1 x 1 x 0.25 mm$^3$, where some are depicted in figure[7].

**B. EDS Analysis**

We measured EDS spectra on several crystals of different batches with different molar amounts of Zn(NO$_3$)$_2$. For this compound evaluable intensity is only caused by Zn, Cu, and O and we found a stoichiometry Zn$_x$Cu$_{4-x}$(OH)$_6$(NO$_3$)$_2$ with a variation of the Zn to Cu ratio, depending on the initial content of Zn(NO$_3$)$_2$ in the solution. Some examples of the substitution amount vs Zn(NO$_3$)$_2$ amount are given in table III which show a nearly linear increase controlled by the molar ratio, similar as for herbertsmithite, where a strong excess of Zn$^{2+}$ ions is necessary to reach substitutions of $x = 1$.

| $<x_{Zn}>$ | 2 | 2.5 | 3 | 4 |
|-----------|---|-----|---|---|
| Zn(NO$_3$)$_2$·6 H$_2$O | g | 0.32(9) | 0.50(12) | 0.61(9) | 0.86(4) |

**TABLE III.** Results of substitution amounts obtained by EDS analysis on single crystals of different batches prepared with different molar amounts of Zn(NO$_3$)$_2$. The error for $x_{Zn}$ is a statistical one, obtained by measuring several spots on several crystals from the same batch.

**C. Structure**

From table III it can be seen, that presently two variants in that family with the NO$_3$ anion were reported in literature. Rouaite, Cu$_4$(OH)$_6$(NO$_3$)$_2$ with space group P2$_1_1$ and CdCu$_3$(OH)$_6$(NO$_3$)$_2$ with space group P3m1 similar to haydeite. It is difficult to differentiate Zn and Cu from X-rays,
The structure is shown along the b-axis compared to the a-axis of haydeite with Mg changed to Cu as it is chosen for the P2₁ structure. From the image one can easily see the similar arrangement of the A ions and the comparable positions of Cl and NO₃. Thus a similar structure is expected for Zn₂Cu₄₋ₓ(OH)₆(NO₃)₂ as depicted in figure S(c). To differentiate between Zn and Cu resonant X-rays are necessary to find the correct subgroup.

We performed magnetic measurements on various ZnₙCu₄₋ₓ(OH)₆(NO₃)₂ single crystals. We found that for concentrations 0.3 < x < 0.9 the magnetic behavior and the ordering temperature is only slightly changed with varying x. In figure 8 we show exemplarily the measurement on a single crystal with x = 0.6. The overall anisotropy is very small, as can be seen from the magnetization at 2 K up to 9T, where both curves for field parallel and perpendicular to the kagome completely overlap. The susceptibility at 0.1 T shows a well-defined anomaly at Tₐ = 7.5 K indicating the onset of antiferromagnetic order. The field dependence of the susceptibility below Tₐ shows a small anisotropy for magnetic fields below 3 T, this is also reflected in small metamagnetic transitions in M(H) in this field range.

From a √χT plot (not shown) the effective moment values of μ_eff || = 1.62μ_B and μ_eff ⊥ = 1.65μ_B at 350 K can be derived. A Curie-Weiss fit of the x = 1 powder sample is shown in figure 8(b) and a Curie-Weiss temperature of Θₜ = 5K, which indicates contributions both from ferromagnetic and antiferromagnetic exchange couplings.

The M(H) curve above 3 T reveals nearly perfect linear behavior with a polarized moment of about 0.3μ_B at 9T, still well below the saturated moment of 1μ_B per Cu²⁺. The overall shape of the M(H) curve confirms the antiferromagnetic nature of the ordered state.

D. Magnetic susceptibility

The distances are d_{A−A} = 3.0648(4) Å of the Cu atoms in the kagome plane and d_{A−A} = 6.9271(9) Å between the AA stacked planes. The angle for the dominant superexchange is θ(Cu1-O1-Cu1) = 104.07(12)°. The atomic positions are given in table IV.

| x/a   | y/b   | z/c   | Occ. U_{iso} Site Sym. |
|-------|-------|-------|------------------------|
| A1    | 0.49908 | 0.50073 | 0.49403 1 0.007 2a 1 | |
| A2    | -0.01041 | 0.25265 | 0.50224 1 0.007 2a 1 | |
| O1    | 0.3664  | 0.7556  | 0.3577 1 0.009 2a 1 | |
| H1    | 0.384   | 0.773   | 0.240 1 0.014 2a 1 | |
| O2    | 0.8141  | 0.5099  | 0.3755 1 0.008 2a 1 | |
| H2    | 0.819   | 0.513   | 0.255 1 0.012 2a 1 | |
| O3    | 0.1877  | 0.4984  | 0.6212 1 0.009 2a 1 | |
| H3    | 0.194   | 0.483   | 0.743 1 0.013 2a 1 | |
| O4    | 0.2937  | 0.2596  | 0.2789 1 0.013 2a 1 | |
| O5    | 0.1092  | 0.1561  | 0.0086 1 0.031 2a 1 | |
| O6    | 0.4036  | 0.3871  | 0.0063 1 0.026 2a 1 | |
| N1    | 0.2680  | 0.2675  | 0.0942 1 0.015 2a 1 | |

TABLE IV. Structural table obtained by refining (occupation fixed to 1) the single crystal diffraction data on a Zn₉Cu₃.₄(OH)₆(NO₃)₂ single crystal measured at 173 K. Using the monoclinic P2₁ ( #4) structure with a unit cell of a = 5.5704(6) Å, b = 6.1274(7) Å and c = 6.9271(8) Å, α = γ = 90°, β = 93.782(9)°.

FIG. 8. a) Picture of the Zn₉Cu₃.₄(OH)₆(NO₃)₂ structure viewed along the b-axis. b) Picture of the haydeite structure viewed along the a-axis. The colorcode is: A = Zn, Cu, Mg (orange), O (red), Cl (green), N (grey) and H (white). c) Picture of the haydeite structure viewed along the c-axis now with Mg in pink.

FIG. 9. The image shows the magnetic data on a Zn₉Cu₃.₄(OH)₆(NO₃)₂ single crystal with a mass of 2.23 mg of the susceptibility in the range of 1.8 - 350 K field cooled at 0.1 - 9T with the field aligned (black dots) and perpendicular to the kagome plane (red dots). a) Inverse susceptibility (M/H)⁻¹ measured on a powder sample of 49.1 mg. b) M(H) curve at 2 K for both field directions, which lay nearly perfectly on each other.
E. Specific heat

We measured the magnetic transition on a single crystal by specific heat. Shown is a measurement within 1.8 K and 15 K on a single crystal with \( x = 0.6 \) and a mass of 8.61 mg. The specific heat curve divided by temperature is shown in figure 10 for fields from 0 up to 9 T. We roughly estimated was measured both along \( \theta \) and perpendicular to the plane of 0, 1, 3, 6 and 9 T from 1.8 to 25 K on a linear fit of a \( C/T vs. T^2 \) plot. With \( \beta = 0.800(6) \text{ mJ/mol K}^2 \) we get an estimated debye temperature of \( \Theta_D \approx 387 \text{ K} \). We observe a pronounced peak at \( T_N \), which is slowly shifted to lower temperatures with increasing fields and reaches 5 K at 9 T. The ordered fraction connected to the anomaly is much higher, compared to the EuCu\(_3\)(OH)\(_6\)Cl\(_3\) system and proves that ZnCu(OH)\(_6\)(NO\(_3\))\(_2\) is only slightly geometrically frustrated, which is in agreement with the small frustration coefficient from the magnetic data.

![Figure 10](image)

FIG. 10. Specific heat measurements in an external field perpendicular to the plane of 0, 1, 3, 6 and 9 T from 1.8 to 25 K on a single crystal of 5.1 mg. A clear anomaly is visible at the magnetic ordering temperature.

V. MgCu\(_3\)(OH)\(_6\)Cl\(_2\)

A. Synthesis

So far reports on the synthesis of haydeeite powder samples were only on a reflux setup with oxygen flushing \[37\]. Here we present a simple way to produce polycrystalline haydeeite MgCu\(_3\)(OH)\(_6\)Cl\(_2\) samples using a reaction of 1 g MgCl\(_2\)-4 H\(_2\)O and 1.16 g CuO heated to 220°C for three days in a Parr 4749 acid digestion vessel. The synthesis is enabled due to the low dissociation temperature of MgCl\(_2\)-4 H\(_2\)O at 110°C. Single crystals could then be prepared by the external gradient method using the prereacted powder as a starting material being dissolved in a solution of 6 g MgCl\(_2\)-4 H\(_2\)O and 5 ml distilled water. The solution was optimized by another pre reaction method of 6 g MgCl\(_2\)-4 H\(_2\)O dissolving 0.48 g CuO in 5 ml water at 220°C for three days leading up to 100 \( \mu \)m haydeeite crystals. It turned out, that the temperature window for the crystallization of haydeeite is narrow. We found 180°C to be the optimal temperature at the cold end, since the polymorphic tondiite Mg\(_x\)Cu\(_{4-x}\)(OH)\(_6\)Cl\(_2\) crystals are formed during the synthesis below 180°C. These tondiite crystals grow even up to 100 mg with 4 x 4 x 3 mm\(^3\) (see figure \[11\]c). But they have an extremely low substitution amount of Mg (0.05 < \( x < 0.4 \)) due to the high MgCl\(_2\) concentration being optimized for haydeeite. Similar to herbertsmithite higher MgCl\(_2\) concentrations lead to a decreased Mg content in the formed tondiite crystals. With a gradient of 200°C - 180°C in a 15 cm ampoule we succeeded to grow hexagonal blue single crystals of up to 0.5 x 0.5 x 0.25 mm\(^3\) and 1.6 mg depicted in figure \[11\]a, b).

![Figure 11](image)

FIG. 11. a), b) Picture of haydeeite crystals grown in an external gradient. c) Images of the parasitic tondiite crystals which dominantly grow below 180°C.

B. EDS Analysis

We measured EDS in the SEM on several crystals of different batches and found a rather high uncertainty for Mg-Cu with this method. To get a grasp of the Mg content we performed electron probe micro analysis (EPMA) on up to four crystals of two different batches. We found an enhanced average substitution content of \( x_{Mg} = 1.2 \pm 0.2 \), compared to even stronger enhanced values with \( x_{Mg} = 1.49 \pm 0.16 \) reported in Ref. \[37\].

C. Magnetic susceptibility

Magnetic and neutron scattering experiments on polycrystalline haydeeite revealed a ferromagnetic ground state below \( T_C = 4.2 \text{ K} \) \[57\]. Here, we present the magnetic measurements on a single crystal with a mass of 0.3 mg. The susceptibility shown in figure \[12\] was measured both along and perpendicular to the kagome plane and reveals a small anisotropy below \( T_C \). The sample shows a ferromagnetic order around 4.3 K with a sizeable field dependence stabilizing the magnetic order as expected for a ferromagnet. From a \( \sqrt{T} \sim \mu_{\text{eff}} \) plot shown in the inset of figure \[12\] the effective moment value of \( \mu_{\text{eff}} = 1.9 \mu_B \) at 290 K can be derived.
c) and confirms the ferromagnetic nature of the compound for fields of 0, 0.1, 0.5, 1, 2, 3 and 4 T along the kagome plane. We observe an ordered moment of $M$ at a field of 0.1 T applied parallel to the kagome plane. The inset shows the inverse susceptibility in the range of 1.8 - 300 K field cooled at 0.1 - 1 T which shows a strong field dependance. We roughly estimated the contributions in a plot of the temperature dependent susceptibility at various fields. The inset is a rescaling on the effective moment by a $\sqrt{T}$ plot of the 50 Oe curve. The magnetization curve in the ordered phase at 1.9 K shown in figure 13 confirms the ferromagnetic nature of the transition. We observe an ordered moment of $M_s = 1 \mu_B$ for both field directions, with the easy axis within the kagome plane, where the saturation is reached around 0.1 T. For field perpendicular to the kagome plane, the critical field is around 2 T. We were not able to resolve a finite hysteresis curve properly. We note that the ordered moment is larger than reported in [56], there an ordered moment of $0.28 \mu_B$ (at 500 Oe) and $M_s = 0.83 \mu_B$ per mole of Cu, was reported. The reason might be slightly different $x$ values. A Curie-Weiss fit of a stack of single crystals for a field applied parallel to the kagome plane is shown on the inset of figure 13 c) and yields Curie-Weiss temperatures of $\Theta^\parallel = 26 \pm 3 K$ compared to $\Theta^\perp = 28 \pm 3 K$. We were not able to resolve a finite hysteresis curve. A Curie-Weiss fit of a stack of single crystals for a field applied parallel to the kagome plane is shown on the inset of figure 13 c) and yields Curie-Weiss temperatures of $\Theta^\parallel = 26 \pm 3 K$ compared to $\Theta^\perp = 28 \pm 3 K$.

D. Specific heat

The observed magnetic transition was also analyzed on several crystals by specific heat. In figure 14 we show a measurement between 1.8 K and 20 K on a single crystal of 0.3 mg. The specific heat curve divided by temperature is shown in figure 14 for fields of 0, 0.1, 0.5, 1, 2, 3 and 4 T along the kagome plane. We roughly estimated the contributions in a temperature range of 15 - 32 K from a linear fit of a C/T vs $T^2$ plot. With $\beta \approx 0.402(7) mJ/molK^{-2}$ we get an estimated debye temperature of $\Theta_D \approx 443 K$. We observe a sharp peak at the magnetic transition, which can best be seen in the $C/T$ plot in figure 14 which shows a strong field dependence shifting it up to 10 K at 4 T. The increased area under the peak compared to the two previously shown compounds is in agreement with the full captured moment in the $M(H)$ curve.

VI. CONCLUSION

In conclusion we have presented results on three members of two-dimensional kagome quantum spin systems in the atacamite family. The successful hydrothermal synthesis of single crystals for these three candidates has been...
shown. They reveal very different magnetic ground states. EuCu$_3$(OH)$_6$Cl$_3$ is a kapellasite-like kagome material with the highest reported Curie-Weiss temperature for the atacamite family of -400 K and presents the strongest anisotropy in this family of up to 2.7 due to Van Vleck paramagnetic Eu$^{3+}$ contributions. The system is strongly frustrated with partial order at 14.7 K and a spin reorientation at 8.7 K. The frustration coefficient is around 30. ZnCu$_3$(OH)$_6$(NO$_3$)$_2$ turned out to be an antiferromagnetic system without strong frustration effects. Magnetic measurements on single crystals revealed only tiny anisotropy in this compound. Furthermore, we present measurements on single crystals of haydeeite and confirmed the ferromagnetic order at 4.3 K measured previously on polycrystals. We detect a small but well-defined anisotropy in the ordered phase with the easy axis within the kagome plane. In addition the specific-heat measurements reveal a clear anomaly, confirming the absence of sizeable frustration effects.

These results together with a compilation of the physical and structural properties of kagome materials around the atacamite family shows us a rich playground where the perfect spin liquid candidate is in close reach. The clue to the latter might be in a more in-depth study of the delicate interplay of the different magnetic exchange couplings. The materials presented in this study give a firm basis to study this influence on the overall degree of frustration in kagome quantum spin systems. Finally, from the presented kagome systems and the listed ones one can assume that an increasing separation of the kagome plane does not stabilize the spin liquid properties.

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[1] L. Balents, *Spin liquids in frustrated magnets*, Nature 464, 199 (2010).
[2] M. P. Shores, E. A. Nytko, B. M. Barlett, and D. G. Nocera, *A structurally perfect S = (1/2) kagomé antiferromagnet*, J. Am. Chem. Soc. 127, 13462 (2005).
[3] J. S. Helton, K. Matan, M. P. Shores, E. A. Nytko, B. M. Barlett, Y. Yoshida, Y. Takano, A. Suslov, Y. Qiu, J.-H. Chung, D. G. Nocera, and Y. S. Lee, *Spin Dynamics of the Spin-1/2 Kagome Lattice Antiferromagnet ZnCu$_3$(OH)$_6$Cl$_2$*, Phys. Rev. Lett. 98, 107204 (2007).
[4] P. Mendels, F. Bert, M. A. de Vries, A. Olariu, A. Harrison, F. Duc, J. C. Trombe, J. S. Lord, A. Amato, and C. Baines, *Quantum Magnetism in the Paratcamite Family: Towards an Ideal Kagomé Lattice*, Phys. Rev. Lett. 98, 077204 (2007).
[5] M. A. de Vries et al., *Extension of the zinc paratcamite phase diagram: Probing the effect of spin vacancies in an S = 1/2 kagome antiferromagnet*, Phys. Rev. B 85, 014422 (2012).
[6] Tian-Heng Han, M. R. Norman, Wen, Jose A. Rodriguez-Rivera, Joel S. Helton, Collin Broholm, and Young S. Lee, *Correlated impurities and intrinsic spin-liquid physics in the kagome material herbertsmithite*, Phys. Rev. B 94, 060409(R) (2016).
[7] M. R. Norman, *Colloquium: herbertsmithite and the search for the quantum spin liquid*, Rev. Mod. Phys. 88, 041002 (2016).
[8] I. I. Mazin, H. O. Jeschke, F. Lechermann, H. Lee, M. Fink, R. Thomale, and R. Valentí, Nat. Comm. 5, 4261 (2014).
[9] P. Puphal, M. Bolte, D. Sheptyakov, A. Pustogow, K. Kliemt, M. Dressel, M. Baenitz, and C. Krellner, *Strong magnetic frustration in Y$_2$Cu$_9$(OH)$_6$Cl$_6$: a distorted kagome antiferromagnet*, J. Mater. Chem. C 5, 2629-2635 (2017).
[10] W. Sun, Y. Huang, S. Nokhrin, Y. Pan and J. Mi, *Perfect Kagomé lattices in YCu$_3$(OH)$_6$Cl$_6$: a new candidate for the quantum spin liquid state*, J. Mater. Chem. C 4, 8772-8777 (2016).
[11] W. Sun, Y. Huang, Y. Pan and J. Mi, *Strong spin frustration and negative magnetization in LnCu$_3$(OH)$_6$Cl$_3$ (Ln = Nd and Sm) with triangular lattices: the effects of lanthanides*, Dalton Trans. 46, 9535-9541 (2017).
[12] H. R. Oswald and W. Feitknecht, *Über die Hydroxydihalogenide Me$_2$(OH)$_3$Cl, -Br, -J zweiwertiger Metalle (Me = Mg, Ni, Co, Cu, Fe, Mn)*, Helv. Chim. Acta 47, 272-289 (1964).
[13] T.-T. Zhu, W. Sun, Y.-X. Huang, Z.-M. Sun, Y. Pan, L. Balents and J.-X. Mi, *Strong spin frustration from isolated triangular Cu(II) trimers in SrCu(OH)$_3$Cl with a novel cuprate layer*, Mater. Chem. C 2, 8170 (2014).
[14] Y. Li, B. Pan, S. Li, W. Tong, L. Ling, Z. Yang, J. Wang, Z. Chen, Z. Wu and Q. Zhang, *Gapless quantum spin liquid in the S = 1/2 anisotropic kagome antiferromagnet ZnCu$_3$(OH)$_6$SO$_4$, New Journal of Physics 16, 093011 (2014).*
[15] R.D. Shannon and C.T. Prewitt, *Effective Ionic Radii in Oxides and Fluorides*, Acta Cryst. B 25, 925 (1969).
[16] R. D. Shannon, *Revised Effective Ionic Radii and Systematic Studies of Interatomic Distances in Halides and Chalco- genides*, Acta Cryst. A 32, 751 (1976).
[17] H.D.B. Jenkins and K.P. Thakur, *Reappraisal of Thermochromical Radis for Complex Ions*, J. Chem. Educ. 56 (9), 576 (1979).
[18] X. G. Zheng, T. Mori, K. Nishiyama, W. Higemoto, H. Yamada, K. Nishikubo, and C. N. Xu, *Antiferromagnetic transitions in polymorphous minerals of the natural cuprates atacamite and botallackite Cu$_2$Cl(OH)$_3$, Phys. Rev. B 71, 174404 (2005).*
[19] X. G. Zheng, T. Kawae, Y. Kashitani, C. S. Li, N. Tateiwa, K. Takeda, H. Yamada, C. N. Xu, and Y. Ren, *Unconventional magnetic transitions in the mineral clinoatacamite Cu$_2$Cl(OH)$_3$, Phys. Rev. B 71, 052409 (2005).*
[20] S. Chu, P. Müller, D. G. Nocera, and Y. S. Lee, *Hydrothermal growth of single crystals of the quantum magnets: Clinoatacamite, paratcamite and herbertsmithite*, Appl. Phys. Lett. 98, 092508 (2011).
[21] S. Vilminot, M. Richard-Plouet, G. André, D. Swierzynski, F. Bourée-Vigneron and M. Kurmoo, *Nuclear and magnetic structures and magnetic properties of synthetic brochantite, Cu$_4$(OH)$_6$SO$_4$, Dalton Trans. 0, 1455-1462 (2006).*
[22] Emily A. Nytko, *Synthesis, structure, and magnetic properties of spin-1/2 kagomé antiferromagnets*, PhD thesis at MIT (2008).
[23] H. Effenberger, *Verfeinerung der Kristallstruktur des monoklinen Dikupfer(II)-trihydroxi-nitrates Cu$_2$(NO$_3$)$_3$(OH)$_3$, Zeitschrift für Kris. 165, 127-135 (1983).*
[24] P. C. Burns, M. A. Cooper, F. C. Hawthorne, *Claringbultite, a Cu$^{2+}$ oxysalt with Cu$^{2+}$ in trigonal-prismatic coordination*, Canadian Min. 33, 633-639 (1995).
[25] T. Han, J. Singleton, and J. A. Schlueter, *Barlowite: A Spin-1/2 Antiferromagnet with a Geometrically Perfect Kagome*
C.M. Pasco, B.A. Trump, Thao T. Tran, Z.A. Kelly, C. Hoffmann, I. Heinmaa, R. Stern, T.M. McQueen, Single crystal growth of Cu$_4$(OH)$_6$Br$_2$ and universal behavior in quantum spin liquid candidates synthetic barlowite and herbertsmithite, arXiv 1801.05769 (2018).

P. Elliott, M.A. Cooper, A. Pring, Barlowite, Cu$_4$FBr(OH)$_6$, a new mineral isostructural with claringbullite: description and crystal structure, Min. Mag. 78, 1755-1762 (2014).

M.D. Welch, M.J. Sciberras, P.A. Williams, P. Leverett, J. Schütter, T. Malcherek, A temperature-induced reversible transformation between paratacamite and herbertsmithite, Phys. Chem. Min. 41, 33-48 (2014).

Pascal Puphal, Ranjith Kumar, Max Muller, Edwin Kermarrec, Denis Sheptyakov, Fabrice Bert, Michael Baenitz, Philippe Mendels, and Cornelius Krellner, GaxCu$_{1-x}$(OH)$_6$Cl$_2$: Insulating ground state in an electron-doped kagome system, to be published (2018).

Y.-S. Li and Q.-M. Zhang, Effect of Zn doping on the antiferromagnetism in kagome lattice Ni$_2$(OH)$_6$Cl$_2$, Canadian Mineralogist 55 (1993).

T. Okuma, Y. Huang, Y. Pan, J. Mi, Synthesis and magnetic properties of centennialite: a new S = ½ Kagome antiferromagnet and comparison with herbertsmithite and kapellasite, Phys. Chem. Minerals 43, 127-136 (2016).

H. Yoshida et al., Unusual Magnetic State with Dual Magnetic Excitations in the Single Crystal of S = 1/2 Kagome Lattice Antiferromagnet CaCu$_{3}$(OH)$_6$Cl$_2$:0.6 H$_2$O, J. Phys. Soc. Jpn. 86, 033704 (2017).

H. Yang, I. F. Barton, M. B. Andrade and R. T. Downs, Crystal structure of a new compound, Cu$_4$ZnCl(OH)$_3$, isostructural with botallackite, American Mineralogist 101, 986-990 (2016).

X.G. Zheng, M. Hagihala, K. Nishiyama, T. Kawae, Exotic antiferromagnetic transition in deformed pyrochlore lattice Ni$_2$(OH)$_4$Cl of atacamite-structure, Phys. B: Cond. Mat. 404, 5-7 (2009).

M. Hagihala, X. G. Zheng, T. Toriyi and T. Kawae, Antiferromagnetism and geometric frustration in tetrahedral lattice hydroxyhalides M$_2$(OH)$_4$X, J. Phys.: Cond. Mat. 19, 145281 (2007).

J. Rodriguez-Carvajal, Recent advances in magnetic structure determination by neutron powder diffraction, Physica B 192, 55 (1993).

Stoe and Cie GmbH, X-AREA. Diffractometer control program system (2002).

G. M. Sheldrick, Acta Cryst. A 64, 112-122 (2008).

T. H. Han, J. S. Helton, S. Chu, A. Prodi, D. K. Singh, C. Mazzoli, P. Müller, D. G. Nocera, and Y. S. Lee, Synthesis and characterization of single crystals of the spin-1/2 kagome-lattice antiferromagnets Zn$_x$Cu$_{3}$(OH)$_6$Cl$_2$, Phys. Rev. B 83, 100402(R) (2011).

See Supplemental Material at http://link.aps.org/supplemental/10.1103/PhysRevMaterials.2.063403 for (1) EuCu$_3$(OH)$_6$Cl$_2$ and (2) ZnCu$_{3}$(OH)$_6$(NO$_3$)$_2$.

S. Seiró, K. Kummer, D. Vynilikh, N. Caroca-Canales, and C. Geibel, Anomalous susceptibility in single crystals of EuCu$_3$S$_4$I$_2$ with trivalent Eu: Influence of excited J multiplets, Phys. Status Solidi B 250, 621–625 (2013).

M. Tovar, D. Rao, J. Barnett, B.S. Oseroff, J.D. Thomson, S-W. Cheong, Z. Fisk, D.C. Vier and S. Schultz, Eu$_2$Cu$_4$O$_9$: An anistropic Vanleck paramagnet, Phys. Rev. B 39, 2661 (1989).

Y. Yamaguchi, S. Waki, M.Tokumoto and K.Hayashi, Crystal-field effect on magnetic susceptibility of EuBa$_2$Cu$_3$O$_y$, Solid State Comm. 66, 1079-1083 (1988).

H. Lueken, Magnetochemie, Teubner Stuttgart, Leipzig 1999.

D. Boldrin, B. Fak, M. Enderle, S. Bieri, J. Ollivier, S. Rols, P. Manuel, and A. S. Wills, Haydedite: A spin-1/2 kagome ferromagnet, Phys. Rev. B 91, 220408(R) (2015).