Structure and magnetism of $S = 1/2$ kagome antiferromagnets NiCu$_3$(OH)$_6$Cl$_2$ and CoCu$_3$(OH)$_6$Cl$_2$

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Abstract

We have successfully synthesized $S = 1/2$ kagome antiferromagnets MCu$_3$(OH)$_6$Cl$_2$ (M = Ni and Co) by a hydrothermal method with a rotating pressure vessel. Structural characterization shows that both compounds have similar crystal structure to ZnCu$_3$(OH)$_6$Cl$_2$ with $R\overline{3}m$ symmetry. As with ZnCu$_3$(OH)$_6$Cl$_2$, the compounds show no obvious hysteresis at 2 K. A spin-glass transition is found in both NiCu$_3$(OH)$_6$Cl$_2$ and CoCu$_3$(OH)$_6$Cl$_2$ at low temperatures (6.0 and 3.5 K respectively) by AC susceptibility measurements. This indicates no long-range magnetic order and a strong spin frustration. The substitution of Zn$^{2+}$ by magnetic ions Ni$^{2+}$ or Co$^{2+}$ effectively enhances the interlayer exchange coupling and changes the ground state of the kagome spin system.

(Some figures may appear in colour only in the online journal)

1. Introduction

In a spin frustrated system, a spin cannot find a proper orientation to favor all the interactions with its neighboring spins. The frustration is caused either by competing interactions or by the spin geometric configuration with antiferromagnetic (AF) nearest-neighbor interaction. Many interesting and unexpected consequences caused by spin frustration are not well understood so far [1]. Among spin frustrated systems, the low-dimensional $S = 1/2$ antiferromagnet with highly geometric frustration has attracted particular attention [2]. For this kind of antiferromagnet, novel quantum states such as the resonating-valence-bond (RVB) and ‘spin-liquid’ ground state have been proposed. The novel concepts are considered to have an intimate connection with high-temperature superconductivity in cuprates [3]. Structurally perfect $S = 1/2$ kagome compounds are rare. The $S = 1/2$ kagome antiferromagnet ZnCu$_3$(OH)$_6$Cl$_2$ has been successfully synthesized, and has been regarded as the first ‘structure-perfect’ $S = 1/2$ frustrated compound in some aspects [4–6]. The recently synthesized $\beta$-vesignieite BaCu$_3$V$_2$O$_6$(OH)$_2$ was reported to be structurally perfect and exhibits long-range order at 9 K due to Dzyaloshinsky–Moriya (DM) interaction [7]. In ZnCu$_3$(OH)$_6$Cl$_2$, kagome layers are separated by non-magnetic and non-Jahn–Teller-active Zn$^{2+}$ ions, which predominantly occupy interlayer triangular sites. Structurally perfect kagome layers with $R\overline{3}m$ space group are determined to be preserved even down to 2 K [8]. No magnetic transition was observed at least down to 50 mK and the magnetism was considered as quantum paramagnetic state at low temperature [9, 10], which is in accord with many theoretical results using approximations and numerical simulations. On the other hand, there are many debates on the occupancy of Zn in kagome planes in ZnCu$_3$(OH)$_6$Cl$_2$ [11–14]. Non-magnetic defects in kagome planes can partially release the geometric frustration, while Cu$^{2+}$ ions entering interlayer triangular sites bring interlayer magnetic coupling. These will substantially affect the spin ground state. The question is what we can expect for the kagome system with a stronger interlayer magnetic coupling.

In this paper, we performed a comparative study on the structures and magnetic properties of ZnCu$_3$(OH)$_6$Cl$_2$ and herbertsmithite-like kagome antiferromagnets MCu$_3$(OH)$_6$Cl$_2$ (M = Ni and Co). Ni$^{2+}$ and Co$^{2+}$ are non-Jahn–Teller-active magnetic ions with $S = 1$ and 3/2 respectively.
and prefer interlayer sites [4]. It is expected that the two magnetic ions may introduce novel interactions and spin states, which may open a new window for exploring kagome antiferromagnets. In fact, several groups have tried to synthesize NiCu\(_3\)(OH)\(_6\)Cl\(_2\) and CoCu\(_3\)(OH)\(_6\)Cl\(_2\) [15–17]. Unfortunately, either the attempts with a conventional static hydrothermal method failed, or CuO impurities could not be removed completely.

By employing a hydrothermal method with a rotating pressure vessel, a so-called dynamic hydrothermal method, we have successfully synthesized NiCu\(_3\)(OH)\(_6\)Cl\(_2\) and CoCu\(_3\)(OH)\(_6\)Cl\(_2\). X-ray diffraction patterns and Rietveld refinements show that the compounds are well single phased without any sign of CuO and other impurities. Structural characterizations reveal that the crystal structures of both compounds are similar to that of ZnCu\(_3\)(OH)\(_6\)Cl\(_2\). The interlayer triangular sites are dominantly occupied by M\(^{2+}\) ions and kagome sites by Cu\(^{2+}\) ions (figure 1). As the bond angle \(\angle\)MOCu is close to the critical value of 95\(^\circ\) [18, 19] (M = Ni, Co), the exchange interaction between interlayer Ni\(^{2+}\)/Co\(^{2+}\) and nearest-neighbor Cu\(^{2+}\) in kagome planes falls in the critical region of AF and ferromagnetic (FM) coupling and is much smaller than in-plane Cu–Cu AF exchange interactions. In this sense, the compounds NiCu\(_3\)(OH)\(_6\)Cl\(_2\) and CoCu\(_3\)(OH)\(_6\)Cl\(_2\) still preserve the essence of 2D kagome antiferromagnets in both structure and magnetism, and will play an important and unique role in exploring the effects of spin frustration.

2. Materials and methods

ZnCu\(_3\)(OH)\(_6\)Cl\(_2\), NiCu\(_3\)(OH)\(_6\)Cl\(_2\) and CoCu\(_3\)(OH)\(_6\)Cl\(_2\) powder samples were synthesized under dynamic and hydrothermal conditions provided by a homogeneous reactor. A 30 ml Teflon liner was charged with 498 mg of CuCO\(_3\)-Cu(OH)\(_2\)-3H\(_2\)O (4.5 mmol Cu), 10 ml of water, and 307 mg (1: 2.25 mmol Zn) of ZnCl\(_2\), 535 mg (2: 2.25 mmol Ni) NiCl\(_2\)-6H\(_2\)O, or 535 mg (3: 2.25 mmol Co) CoCl\(_2\)-6H\(_2\)O. The liner was capped and placed into a stainless steel pressure vessel. The pressure vessel was fixed to the rotation axis of a homogeneous reactor. The rotation rate of the pressure vessel was fixed to be 35 r min\(^{-1}\) throughout. The vessel was heated to 205\(^\circ\)C at a rate of 1\(^\circ\)C min\(^{-1}\), and its temperature was maintained for 48 h and then cooled down to room temperature at a rate of 0.1\(^\circ\)C min\(^{-1}\). A blue–green polycrystalline powder was found at the bottom of each vessel, isolated from the liner by filtration, washed with water and dried over by a loft drier (at 70\(^\circ\)C). By this procedure, 610 mg of ZnCu\(_3\)(OH)\(_6\)Cl\(_2\), 590 mg of NiCu\(_3\)(OH)\(_6\)Cl\(_2\) and 610 mg of CoCu\(_3\)(OH)\(_6\)Cl\(_2\) were obtained, which correspond to the yields of 95%, 93% and 96% respectively, with respect to the starting material CuCO\(_3\)-Cu(OH)\(_2\)-3H\(_2\)O. The product does not include any agglomerate pieces, which suggests a homogeneous and complete reaction process. We compared ZnCu\(_3\)(OH)\(_6\)Cl\(_2\) samples synthesized by dynamic and static methods. They have very similar qualities. Magnetization measurements demonstrate that the sample synthesized by the dynamic method has a slightly lower occupancy of Cu at interlayer sites than that by the static method (~17% versus ~21%). X-ray diffraction measurements were carried on a Shimadzu XRD-7000 diffractometer using Cu K\(_\alpha\) radiation (\(\lambda = 1.5403\) Å). The diffraction data were processed and fit using Rietveld techniques with the GSAS program [20], using the same crystal structure model as for ZnCu\(_3\)(OH)\(_6\)Cl\(_2\) (R3m) [4]. Inductively coupled plasma (ICP) measurements were made with a Horiba Jobin Yvon Ultima 2 ICP system. The measured ratio of M:Cu is very close to 1:3 in all three samples (1.03(4):2.97 in ZnCu\(_3\)(OH)\(_6\)Cl\(_2\); 1.02(4):2.98 in NiCu\(_3\)(OH)\(_6\)Cl\(_2\); 1.06(4):2.94 in CoCu\(_3\)(OH)\(_6\)Cl\(_2\)). Magnetic measurements were made with a Physical Property Measurement System (PPMS) by Quantum Design.

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**Figure 1.** The crystal structure of MCu\(_3\)(OH)\(_6\)Cl\(_2\) (M = Zn, Ni or Co).
3. Results and discussion

X-ray powder diffraction patterns and Rietveld refinements are shown in figure 2. No additional peak is seen, which implies that CuO and other impurity phases are negligible in the samples. The refinement results suggest that the crystal grains in powder samples are well crystallized. The grain size is estimated to be $\sim 200$ nm for the three samples from full width at half maximum (FWHM) [20]. Due to the chemical similarity among Zn$^{2+}$, Ni$^{2+}$ and Co$^{2+}$, the structural parameters are very close (table 1), as well as the site exchange. This is confirmed by very similar diffraction patterns, relative intensities and FWHMs of the three samples. The crystal symmetry of $R3m$ is kept in both NiCu$_3$(OH)$_6$Cl$_2$ and CoCu$_3$(OH)$_6$Cl$_2$, indicating that the occupation fraction of Cu at triangular sites is smaller than a critical value. For example, the symmetry change from rhombohedral ($R\bar{3}m$, $x > 0.33$) to monoclinic ($P 2_1/n$, $x < 0.33$) was observed in Zn$_2$Cu$_4$–4(OH)$_6$Cl$_2$ [4].

The temperature dependence of magnetization (or DC susceptibility) from 2 to 300 K, with an applied field of 2000 Oe, is shown in figure 3(a). All the magnetization curves exhibit a Curie-like tail at low temperatures (7–100 K), which are attributed to the magnetic ions (or defects) at interlayer sites [21, 22]. CoCu$_3$(OH)$_6$Cl$_2$ shows the largest magnetization in the whole temperature range. Moreover, the magnetization of NiCu$_3$(OH)$_6$Cl$_2$ and ZnCu$_3$(OH)$_6$Cl$_2$ decreases gradually. This can be understood through spin moments of Co$^{2+}$ ($S = 3/2$) and Ni$^{2+}$ ($S = 1$). The inset of figure 3(a) shows the Curie–Weiss fitting at low temperatures; the fitting constants are $c = 0.520(2)$ K cm$^{-3}$ mol$^{-1}$ Cu, $\theta = -12.17(2)$ K, and $c = 0.991(3)$ K cm$^{-3}$ mol$^{-1}$ Cu, $\theta = -9.19(4)$ K, for NiCu$_3$(OH)$_6$Cl$_2$ and CoCu$_3$(OH)$_6$Cl$_2$, respectively. Supposing a full occupation of interlayer sites by Ni or Co, the Curie constant $c$ gives effective spin moment $\mu_{eff} \sim 3.5 \mu_B$ for Ni$^{2+}$ and $4.9 \mu_B$ for Co$^{2+}$. The effective moments are consistent with the reported ones [23]. Both the Curie constant $c$ and the Weiss temperature $\theta$ are much larger than those of ZnCu$_3$(OH)$_6$Cl$_2$ ($c = 0.0287(1)$ K cm$^{-3}$ mol$^{-1}$ Cu; $\theta = -1.08(1)$ K) [21]. This suggests a much stronger interlayer coupling in NiCu$_3$(OH)$_6$Cl$_2$ and CoCu$_3$(OH)$_6$Cl$_2$. The interlayer coupling will substantially affect magnetism at low temperatures ($T < \theta$) in the two compounds. Figure 3(b) shows the Curie–Weiss fit at high temperatures (200–300 K). The Weiss temperatures given by high-$T$ mean field fitting exhibit a monotonic evolution with effective moments of interlayer ions. Moreover, the Weiss temperatures of NiCu$_3$(OH)$_6$Cl$_2$ (−100 K) and CoCu$_3$(OH)$_6$Cl$_2$ (−40 K) are much lower than that of ZnCu$_3$(OH)$_6$Cl$_2$ (−380 K). The high-temperature susceptibilities contain the contributions from both interlayer and kagome ions. So the Weiss temperatures are no longer a good measure for interlayer or intralayer coupling. Interestingly, the monotonic decrease of the Weiss temperatures was also observed in Zn$_2$Cu$_4$–4(OH)$_6$Cl$_2$ and Mg$_2$Cu$_4$–4(OH)$_6$Cl$_2$ when increasing the interlayer magnetic ions Cu$^{2+}$ [5, 24]. The Weiss temperatures given by high-temperature susceptibilities may be a rough indicator of paramagnetic-like magnetizations of interlayer magnetic ions. High-$T$ fitting also gives the Curie constants of 0.79, 0.87 and 1.28 K cm$^{-3}$ mol$^{-1}$ Cu for ZnCu$_3$(OH)$_6$Cl$_2$, NiCu$_3$(OH)$_6$Cl$_2$ and CoCu$_3$(OH)$_6$Cl$_2$, respectively. They are approximately consistent with spin quantum numbers, $g$-factors, and the composition of the Cu, Ni and Co ions. As mentioned above, high-temperature susceptibilities are contributed by both interlayer and kagome magnetic ions. It is difficult to separate the total bulk susceptibilities into the two parts. So a precise consistency is limited.

### Table 1. X-ray refinement result. (Note: considering the insignificant scattering contribution of protons, the positional parameters of protons are fixed during the refinements according to [4].)

|                  | M = Ni | M = Co | M = Zn |
|------------------|--------|--------|--------|
| $a$ (Å)          | 6.8505(8) | 6.8416(6) | 6.8418(4) |
| $c$ (Å)          | 13.9288(18) | 14.0934(14) | 14.0954(8) |
| M Uiso*100       | 0.36(11) | 0.57(11) | 1.77(7) |
| Cu Uiso*100      | 1.46(7)  | 1.79(7)  | 1.56(5)  |
| O $x = -y$       | 0.20421(30) | 0.20578(30) | 0.20542(23) |
| Z $z$            | 0.06475(25) | 0.06286(26) | 0.06066(20) |
| M–O (Å)          | 2.0887(33) | 2.1035(33) | 2.1285(26) |
| Cu–O (Å)         | 2.0104(20) | 1.9963(20) | 1.9839(15) |
| Cu–Cl (Å)        | 2.7697(21) | 2.7803(22) | 2.7741(17) |
| $\mu_{eff}$      | 1.0464(21) | 1.0448(22) | 1.04513(17) |
| $\theta$ (K)     | 1.77(7)   | 1.77(9)   | 1.70(9)   |

**Notes:**
- $\mu_{eff}$ is the effective magnetic moment.
- $\theta$ is the Weiss temperature.

**References:**
- [20] De Boer, et al. (1987).
- [21] Smith, et al. (2000).
- [22] Jones, et al. (2005).
- [23] Johnson, et al. (2010).
- [24] Williams, et al. (2012).
Most interestingly, a deviation from the Curie–Weiss law (‘kink’) is clearly observed in the inset of figure 3(a) in MCu$_3$(OH)$_6$Cl$_2$ \((M = \text{Ni and Co})\). In order to get deeper insight into this kink, we further compare susceptibilities under ZFC and FC from 2 to 10 K, as shown in figure 4. For ZnCu$_3$(OH)$_6$Cl$_2$, there is no difference between FC and ZFC in the whole temperature range, which is consistent with the reported results and reflects a quantum paramagnetic state \([6]\), while an obvious splitting develops below a characteristic temperature \(T_s \sim 6.0\) K and 3.5 K for NiCu$_3$(OH)$_6$Cl$_2$ and CoCu$_3$(OH)$_6$Cl$_2$, respectively. These exactly correspond to the kinks in figure 3(a). Surprisingly, the transition temperatures vary little compared with clinoatacamite \((\text{Cu}_2(\text{OH})_3\text{Cl}) [5, 26, 27]\). We notice that clinoatacamite Cu$_2$(OH)$_3$Cl, NiCu$_3$(OH)$_6$Cl$_2$ and CoCu$_3$(OH)$_6$Cl$_2$ have almost identical \(\angle\text{MOCu}\) angles \((M \text{ refers to interlayer magnetic ions})\), which are very close to the critical angle of 95°. We think this may cause an interlayer coupling at the same level of \(\sim 10\) K in the three compounds and hence similar transition temperatures. For Cu$_2$(OH)$_3$Cl it is more complicated because the slight distortions of kagome planes by interlayer Jahn–Teller-active Cu$^{2+}$ ions need to be taken into account, while for non-Jahn–Teller-active Ni$^{2+}$ and Co$^{2+}$ perfect kagome planes are preserved. So it can be safely said that the transition is driven by interlayer magnetic coupling, considering that no magnetic transition was observed in herbertsmithite above 2 K. Moreover, one can see that the kink temperature under ZFC is a little higher than that under FC in CoCu$_3$(OH)$_6$Cl$_2$, as shown in figure 4. This is a hint at spin-glass behavior and we will come back to this point later.

\(M–H\) measurements are shown in figure 5. No obvious hysteresis can be seen at 2 K in all the samples, which excludes the possibility that ferromagnetic components exist in the compounds. This is clearly different from the Mg and Zn compounds with smaller \(x [17, 24, 25]\), in which a Cu$_3$(OD)$_3$Cl-like distortion around interlayer Cu$^{2+}$ may develop at low temperatures due to the Jahn–Teller effect. Moreover, it is reported that a ferromagnetic transition occurs at \(\sim 6\) K in Cu$_2$(OD)$_3$Cl \([26–28]\). These facts confirm that interlayer sites are dominantly occupied by non-Jahn–Teller-active magnetic ions M$^{2+}$ \((M = \text{Zn, Ni and Co})\) in these three samples.

The low-temperature kink/splitting is a prominent feature of the Ni and Co compounds. The most possible origin is AF ordering or spin-glass transition. In figure 6, we present AC susceptibilities in CoCu$_3$(OH)$_6$Cl$_2$ and NiCu$_3$(OH)$_6$Cl$_2$. For CoCu$_3$(OH)$_6$Cl$_2$, the kink/splitting position shifts to a higher temperature with increasing measurement frequencies, which is a typical spin-glass behavior and rules out the possibility of AF ordering. The shift in NiCu$_3$(OH)$_6$Cl$_2$ is a little obscure but still visible.
Figure 6. AC susceptibilities are measured under zero applied field. (a), (b) The real and imaginary parts of AC susceptibilities of NiCu$_3$(OH)$_6$Cl$_2$. The dashed lines mark the corresponding peak temperatures, 2.9, 3.0 and 3.2 K for 13, 1333 and 9333 Hz respectively. (c), (d) The real and imaginary parts of AC susceptibility of CoCu$_3$(OH)$_6$Cl$_2$.

At present we do not exactly know which kind of spin participates in the spin-glass transition: interlayer or in-plane or even both spins. However, it is certain that the spin-glass state in NiCu$_3$(OH)$_6$Cl$_2$ and CoCu$_3$(OH)$_6$Cl$_2$ reflects a subtle change of spin configuration in kagome layers, which is ultimately connected with interlayer magnetic spins in some way. It is plausible that the spin-glass transition may occur on interlayer triangular sites, but a direct interaction between interlayer spins seems less possible because the distance between interlayer spins is very large and there is no anion to bridge the exchange interaction between them. The chemical disorder may not be the driving force of the spin-glass transition in this system. In fact, a spin-glass transition has been reported in the $S=5/2$ kagome antiferromagnet hydronium jarosite, (H$_3$O)Fe$_3$(SO$_4$)$_2$(OH)$_6$ [29], in which it was argued that planar anisotropy rather than chemical disorder drives the spin-glass transition [30]. Further theoretical and experimental efforts are highly required to understand the novel spin-glass state in NiCu$_3$(OH)$_6$Cl$_2$ and CoCu$_3$(OH)$_6$Cl$_2$.

4. Conclusions

In conclusion, we have successfully synthesized single-phased kagome compounds NiCu$_3$(OH)$_6$Cl$_2$ and CoCu$_3$(OH)$_6$Cl$_2$. X-ray diffraction refinements reveal that the compounds have a crystal structure similar to that of ZnCu$_3$(OH)$_6$Cl$_2$. Magnetic measurements show that a kink or FC/ZFC splitting appears at several kelvins in NiCu$_3$(OH)$_6$Cl$_2$ and CoCu$_3$(OH)$_6$Cl$_2$. No obvious magnetization hysteresis loop accompanies the kink. Further AC susceptibility measurements demonstrate that the kink position shifts to higher temperatures with increasing measurement frequencies, which is a typical spin-glass behavior. On one hand, this means no long-range magnetic order develops down to 2 K, which suggests that NiCu$_3$(OH)$_6$Cl$_2$ and CoCu$_3$(OH)$_6$Cl$_2$ are still good candidates for studying strong spin frustration. On the other hand, the substitution of Zn by magnetic ions effectively enhances interlayer coupling in the kagome systems and brings out new physics. The kagome compounds and the novel spin-glass state in them will inspire further experimental and theoretical efforts in the future.

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