Recent developments in the magnetic study of the deformed pyrochlore lattice $M_2$(OH)$_3X$ ($M = 3d$ magnetic ions, $X = \text{Cl, Br}$) - exotic magnetic order in Ni$_2$(OH)$_3$Cl and controlled spin-spin interactions in Co$_2$(OH)$_3$Cl$_{1-x}$Br$_x$ and (Co$_{1-x}$Fe$_x$)$_2$(OH)$_3$Cl

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Abstract. Following the discovery of frustrated magnetism in deformed pyrochlore lattice Cu$_2$(OH)$_3$Cl and Co$_2$(OH)$_3$Cl we have extensively investigated the material series in the chemical formula of $M_2$(OH)$_3X$, with $M = \text{Cu, Co, Ni, Fe, Mn, and } X = \text{Cl, Br, or I}$. In atacamite-structure Ni$_2$(OH)$_3$Cl, strong geometric frustration and an exotic antiferromagnetic transition below 5 K was found. While neutron diffraction witnessed unambiguously an antiferromagnetic long-range order, the $\mu$SR method can’t “see” this order, instead, the detected local field behaved quite like a dynamically fluctuating one. For the system of Co$_2$(OH)$_3$Cl, the magnetic state is very sensitive to both the anion and cation substitution. While Co$_2$(OH)$_3$Cl behaves like a zero-field kagomé ice ferromagnet, a completely substituted version of Co$_2$(OH)$_3$Br becomes antiferromagnetic although there is little difference in the crystal structure. The antiferromagnetic Co$_2$(OH)$_3$Br showed complicated magnetic transitions. Meanwhile, partially substituted Co$_2$(OH)$_3$Cl$_{1-x}$Br$_x$ transforms from ferromagnetic to antiferromagnetic with increasing the $x$ ratio. The results suggest that the interaction on the kagome-lattice plane is antiferromagnetic while that on the triangular lattice plane is ferromagnetic. For the substituted series (Co$_{1-x}$Fe$_x$)$_2$(OH)$_3$Cl a spin glass state is observed.

1. Introduction

In recent years, we found unconventional magnetic transitions in a mineral compound clinoatacamite Cu$_2$(OH)$_3$Cl [1], wherein we further observed the coexistence of long-range antiferromagnetic order and spin fluctuation [2]. It is the first example of the $S = 1/2$ (Cu$^{2+}$) Heisenberg quantum spin on a pyrochlore lattice and the mother compound for the “perfect kagome lattice” ZnCu$_3$Cl$_2$(OH)$_6$ exhibiting spin liquid behaviour [3].

We further found that in another compound with a similar chemical formula Co$_2$(OH)$_3$Cl, a partial FM order coexists with spin fluctuation [4]. The partial FM order is similar to the field-induced “kagome ice” state in pyrochlore Dy$_2$Ti$_2$O$_7$, i.e., it is a zero-field kagome ice which is thought to be induced by the distorted pyrochlore structure.
There is a rich material series in the chemical formula of $M_2(OH)_3X$, with $M = Cu, Co, Ni, Fe, Mn$, and $X = Cl, Br, or I$. Many chemical formulas have polymorphous crystal structures which can be the deformed pyrochlore lattice [1,4,5], two-dimensional kagome-like lattices or triangular lattice. Up to date we have extensively investigated their magnetic properties with multiple magnetic probes including magnetization, specific heat, neutron diffraction and muon spin relaxation/rotation (μSR). Exotic magnetic properties arising from geometric frustration and complicated phase transitions have been observed for many compounds. The present report concentrates on the atacamite-structure Ni$_2$(OH)$_3$Cl, where a novel antiferromagnetic order was found, and two substituted series of Co$_2$(OH)$_3$Cl$_{1-x}$Br$_x$ and (Co$_{1-x}$Fe$_x$)$_2$(OH)$_3$Cl, which greatly help us to understand the magnetic couplings in the zero-field kagome ice Co$_2$(OH)$_3$Cl.

2. Experimental details

Polycrystalline samples were prepared by hydrothermal reaction of $MX_2$ ($M =$ magnetic ion, $X =$ halogen) and NaOH at around 200°C for several hours. The crystal structures were determined using synchrotron x-ray diffraction at beam line BL02B2, Spring-8. The magnetization was measured using a commercial SQUID magnetometer (MPMS-7). Heat capacity was measured by an adiabatic heat pulse method with a $^3$He cryostat using an amount of approximately 0.7 g of the polycrystals. Muon spin rotation/relaxation (μSR) measurements were carried out at m20 at TRIUMF. Neutron powder diffraction measurements were conducted at HERMES, JAERI using a wave length of 1.8265 Å.

3. Results and discussion

3-1. Ni$_2$(OH)$_3$Cl

Atacamite-type Ni$_2$(OH)$_3$Cl crystallizes in orthorhombic structure (pace group A-62) with lattice parameters $a = 6.1661$ Å, $b = 6.7087$ Å and $c = 9.0528$ Å, respectively, similar to the atacamite Cu$_2$(OH)$_3$Cl [7]. The Ni$^{2+}$ ions are located on the four corners of tetrahedron forming a linked tetrahedral network as shown in figure 1.

![Figure 1](image)

**Figure 1.** The crystal structure of Ni$_2$(OH)$_3$Cl.
Figure 2 shows the temperature dependence of the magnetic susceptibility indicating an antiferromagnetic transition at around $T_N = 5$ K with strong frustration at high temperatures. However, the zero-field $\mu$SR spectra as shown in figure 3 would rather suggest a dynamical local field. Neither the recovery of the asymmetry to the 1/3 of the initial value or any oscillation (on the short-time spectra not shown here), which would appear in a static field, were observed below $T_N = 5$ K. On the other hand, the neutron diffraction pattern clearly showed the development of the magnetic order (figure 4).

![Figure 2](image1)

**Figure 2.** Magnetic susceptibility of Ni$_2$(OH)$_3$Cl.

![Figure 3](image2)

**Figure 3.** The $\mu$SR spectra for Ni$_2$(OH)$_3$Cl.

This unconventional behaviour cannot be explained consistently with a known magnetic order. Very recently Tsuneishi et al. proposed a novel antiferromagnetic order on frustrated tetrahedral lattice, i.e.,
the squared Fourier amplitude orders but the amplitude itself fast fluctuating [8]. The present compound Ni₂(OH)₃Cl might be the first practical material system for this novel order.

![Neutron diffraction pattern](image)

**Figure 4.** The neutron diffraction pattern for Ni₂(OH)₃Cl.

### 3-2. Co₂(OH)₃Br and the series Co₂(OH)₃ClₓBr₁₋ₓ

The Co₂(OH)₃Br compound crystallizes in the same hexagonal structure as that of Co₂(OH)₃Cl with slightly larger unit cell parameters \(a = 6.9717 \text{ Å}, c = 14.664 \text{ Å}\) for Co₂(OH)₃Br compared with \(a = 6.8420 \text{ Å}, c = 14.504 \text{ Å}\) for Co₂(OH)₃Cl. In special, it is featured by longer Co-Co bonding length on the kagome lattice plane due to the larger Br ions [for the detailed structure see ref. 4]. Our recent research on the two dimensional structures of the \(M₂(OH)₃X\) series suggest that the \(M-Br-M\) interaction is stronger than that of \(M-Cl-M\). Hence we suppose that the interaction on the kagome lattice plane in Co₂(OH)₃Br is enhanced as compared with Co₂(OH)₃Cl.

![Ac magnetic susceptibility data](image)

**Figure 5.** The ac magnetic susceptibility data for Co₂(OH)₃Br.
Figure 5 shows the ac magnetic susceptibility data for Co$_2$(OH)$_3$Br, suggesting an antiferromagnetic transition at around 6 K together with multiple relaxation processes. Heat capacity measurement suggested successive transition at $T_{N1} = 6.2$ K and $T_{N2} = 4.8$ K (figure 6). Magnetization curves at 2 K in figure 7 showed additional change at $H \sim 5$ kOe besides the spin-flop at around 17 kOe, suggesting the existence of a field-induced phase at weak field.
By a detailed comparison with Co$_2$O(OH)$_3$Cl we can conclude that an antiferromagnetic order develops in Co$_2$(OH)$_3$Br due to the enhanced magnetic bonding on the kagome lattice plane, meanwhile, this antiferromagnetic order is liable to be transformed in a magnetic field into a ferromagnetic order, which is considered as a result of the promoted ferromagnetic coupling along the $c$-axis for the magnetic ions on the triangular lattice planes.

The results of anion substitution in Co$_2$(OH)$_3$Cl$_{1-x}$Br$_x$ support this surmise. Pure phase samples for $0 < x < 1$ were successfully synthesized. Figure 8 shows the susceptibility data for several compositions. The Curie-Weiss temperatures are plotted in figure 9, suggesting the FM to AFM transition at around $x = 0.64$.

![Figure 8](image1.png)

**Figure 8.** Magnetic susceptibility data for Co$_2$(OH)$_3$Cl$_{1-x}$Br$_x$.

![Figure 9](image2.png)

**Figure 9.** Phase diagram for Co$_2$(OH)$_3$Cl$_{1-x}$Br$_x$.
3.3. Fe₂(OH)_3Cl and the series (Co_1-x Fe_x)_2(OH)_3Cl

Fe₂(OH)_3Cl also crystallizes in the same hexagonal structure as that of Co₂(OH)_3Cl with slightly larger unit cell parameters \((a = 6.9402 \text{ Å}, \ c = 14.727 \text{ Å})\) for Fe₂(OH)_3Cl). Figure 10 shows the dc magnetic susceptibility data under field-cooling and zero-field-cooling conditions, respectively, for the series \((\text{Co}_{1-x} \text{Fe}_x)_2\text{(OH)}_3\text{Cl})\). As shown by the inset plot Fe₂(OH)_3Cl shows an antiferromagnetic transition at around 9 K. Meanwhile, spin-glass-like freezing was observed for \(x\) ranging from 0.3 to 0.7. The freezing temperatures are plotted in figure 11 together with the transition temperatures of the samples \(x = 0\) and \(x = 1\). For \(x = 0.5\) prominent spin glass behaviours were observed (figure 12).

![Figure 10](image1.png)

**Figure 10.** Magnetic susceptibility data for \((\text{Co}_{1-x} \text{Fe}_x)_2\text{(OH)}_3\text{Cl}).

![Figure 11](image2.png)

**Figure 11.** Phase diagram for \((\text{Co}_{1-x} \text{Fe}_x)_2\text{(OH)}_3\text{Cl}).
In summary, we have extensively investigated the material series $M_2(OH)_3X$ besides Cu$_2$(OH)$_3$Cl and Co$_2$(OH)$_3$Cl. In atacamite-structure Ni$_2$(OH)$_3$Cl, we found an exotic antiferromagnetic transition below 5 K, which may be explained by a recently proposed new antiferromagnetic order on frustrated tetrahedral lattice, i.e., the squared Fourier amplitude orders but the amplitude itself fast fluctuating [8]. For the system of Co$_2$(OH)$_3$Cl, the magnetic state is very sensitive to both the anion and cation substitution. The partially substituted Co$_2$(OH)$_3$Cl$_{1-x}$Br$_x$ transforms from ferromagnetic to antiferromagnetic with increasing the $x$ ratio. The results suggest that the interaction on the kagome-lattice plane is antiferromagnetic while that on the triangular lattice plane is ferromagnetic. For the substituted series (Co$_{1-x}$Fe$_x$)$_2$(OH)$_3$Cl spin glass states were observed in the intermediate regions. More detailed studies with μSR and neutron diffraction are in progress.

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