Antiferromagnetism and geometric frustration in tetrahedral lattice hydroxyhalides $M_2(OH)_3X$

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Abstract

A systematic study of magnetic susceptibility measurements is carried out on distorted tetrahedral lattice hydroxyhalides $Fe_2(OH)_3Cl$, $Mn_2(OH)_3Cl$, $Mn_2(OH)_3Br$, and $Co_2(OH)_3Br$, following our recent finding of coexisting antiferromagnetic order and disorder in $Cu_2(OH)_3Cl$ (clinoatacamite). These transition metal hydroxyhalides are found to undergo antiferromagnetic transitions, at $T_N = 14$ K for $Fe_2(OH)_3Cl$, at two successive transitions of $T_{N1} = 3.4$ K and $T_{N2} = 2.7$ K for $Mn_2(OH)_3Cl$, at $T_{N1} = 3.3$ K and $T_{N2} = 2.4$ K for $Mn_2(OH)_3Br$, and at $T_N = 5$ K for $Co_2(OH)_3Br$, respectively. All hydroxychlorides show coexisting glassiness below the magnetic transitions; meanwhile, the glassiness is not found in the hydroxybromides. The distorted tetrahedral lattice for the magnetic ions consists of stacked layers of triangular lattice planes and Kagome lattice planes, with the magnetic ions on the Kagome lattice planes being bonded by the halogen ions. The contrasting behaviours in $Mn_2(OH)_3Cl$ and $Mn_2(OH)_3Br$ suggest that the glassiness arises from competing magnetic interactions in the tetrahedron, specifically on the Kagome lattice planes.

1. Introduction

Geometrically frustrated magnetic systems have been of intense recent interest because of their exotic ground states [1]. A common property is disorder or glassiness that arises from competing interactions. A model frustrated system is found in the rare-earth pyrochlore lattice, of which even its ferromagnetic members (e.g. $Ho_2Ti_2O_7$) are intensely frustrated [2], as a magnetic equivalent of the ice model, and its antiferromagnetic (AF) members (e.g. $Tb_2Ti_2O_7$) are strongly frustrated, to be proposed as candidates for the experimental realization of the spin liquid [3].

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Recently, we obtained experimental evidence in muon spin rotation/relaxation (μSR) that long range order can coexist with spin fluctuation in a clean compound of $Cu_2(OH)_3Cl$ (clinoatacamite). Clinoatacamite shows a three-dimensional network of corner-sharing tetrahedrons of Cu^{2+} spins in a monoclinic lattice. The tetrahedron-like coordination of the Cu^{2+} ions resembles that of the pyrochlores except that the tetrahedron in the $Cu_2(OH)_3Cl$ is slightly tilted [4, 5]. A long-range antiferromagnetic (AF) order develops at $T_{N1} = 18.1$ K with a very small entropy drop ($\sim 0.1 \ln 2/Cu$), and at lower temperatures the long-range order suddenly gives way to a dynamic fluctuating state. Then the freezing of the magnetic moment appears and the system transits into coexisting states of long range order and fluctuation. In magnetic susceptibility measurements, glassiness appears together with the second transition at $T_{N2} = 6.4$ K. Unlike the pyrochlores, where a dipolar coupling between the f-electron rare-earth ions with large magnetic moments and the orbital effect must be considered, the spin-only magnetism of $Cu_2(OH)_3Cl$ represents ideal realization of the frustrated Heisenberg antiferromagnet. The unusual coexisting state of long-range order and fluctuation is considered to be a new quantum state.

In order to clarify this unusual quantum spin state, besides experiments under various external conditions (such as pressure, strong magnetic field etc), it is useful to explore the magnetic states and their changes by replacing the magnetic ions with different ones. Therefore, it is of strong interest whether other d-electron transition metal magnetic ions on this tetrahedral lattice also show such magnetic behaviour. It is obvious that a systematic study of this material system would greatly help in gaining insight into the fascinating quantum state exhibited by $Cu_2(OH)_3Cl$ so that we can unveil the underlying physics. This work reports the first measurement of the magnetic properties of tetrahedral lattice hydroxyhalides $Fe_2(OH)_3Cl$, $Mn_2(OH)_3Cl$, $Mn_2(OH)_3Br$, and $Co_2(OH)_3Br$. To date, some of these compounds have been found to exist in minerals; however, their magnetic properties have not been reported.

2. Experimental details

Polycrystalline samples were prepared by hydrothermal reaction of MX_2 (M = magnetic transition metal ion, X = halogen) and NaOH at around 200 °C for several hours. X-ray diffraction experiments suggested that $Fe_2(OH)_3Cl$ and $Co_2(OH)_3Br$ have the same structure as $Co_2(OH)_3Cl$ in rhombohedral, $R\bar{3}m$ [6], while $Mn_2(OH)_3Cl$ and $Mn_2(OH)_3Br$ show the structure of atacamite $Cu_2(OH)_3Cl$ in orthorhombic, $Pnma$ [7]. All of them feature a tetrahedron-like coordination of the magnetic ions as we previously reported for $Cu_2(OH)_3Cl$ [4].

The temperature dependence of magnetic susceptibility, the magnetization under zero field cooling (ZFC) and field cooling (FC) conditions, and the field dependence of the magnetization ($M-H$) were measured using a commercial SQUID magnetometer (MPMS-7). The zero-field measurements were actually carried out in a remnant field of approximately 6 Oe. Heat capacity was measured for $Mn_2(OH)_3Cl$ by an adiabatic heat pulse method with a ^{3}He cryostat using an amount of 0.7 g of the polycrystals.

3. Results and discussion

The temperature dependence of magnetic susceptibility $\chi \equiv M/H$ at $H = 1$ kOe upon field cooling and its reciprocal for $Fe_2(OH)_3Cl$ are shown in figure 1. Antiferromagnetic transition was observed at $T_N = 14$ K. The small hump seen around 140 K in the plot was assumed to be due to impurity phases because the surfaces of the polycrystalline grains were confirmed to get quickly oxidized in air. Taking this effect into consideration, the susceptibility is analysed
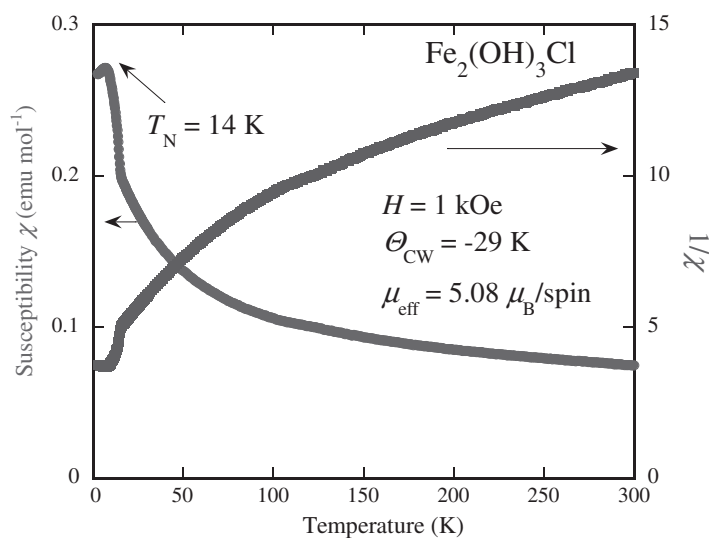
Figure 1. Temperature dependence of the magnetic susceptibility $\chi \equiv M/H$ and its reciprocal at $H = 1$ kOe upon field cooling for $Fe_2(OH)_3Cl$.

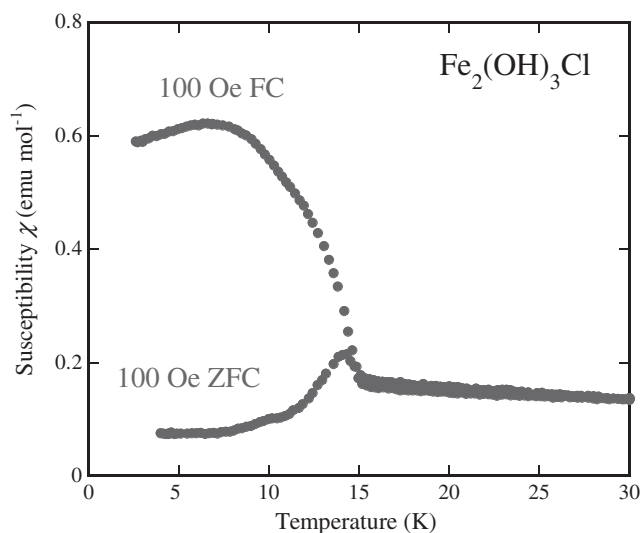**Figure 2.** Temperature dependence of the susceptibility at 100 Oe under ZFC and FC conditions for $Fe_2(OH)_3Cl$.

by the formula $\chi = \chi_0 + C/(T - \Theta_{cw})$, where Θ_{cw} is the paramagnetic Curie temperature. A Θ_{cw} of -29 K and an effective magnetic moment of 5.08 μ_B are estimated for $Fe_2(OH)_3Cl$. In figure 2 the susceptibility curves at weak field of 100 Oe under ZFC and FC conditions are shown, which suggest coexisting glassiness below the antiferromagnetic transition. Like the situation in clinoatacamite $Cu_2(OH)_3Cl$ [5], the glassiness coexists with the antiferromagnetic order, therefore producing the increase in the susceptibility below the T_N in figure 1. The field dependence of the magnetization $M-H$ in figure 3 supported the antiferromagnetic nature below 14 K.
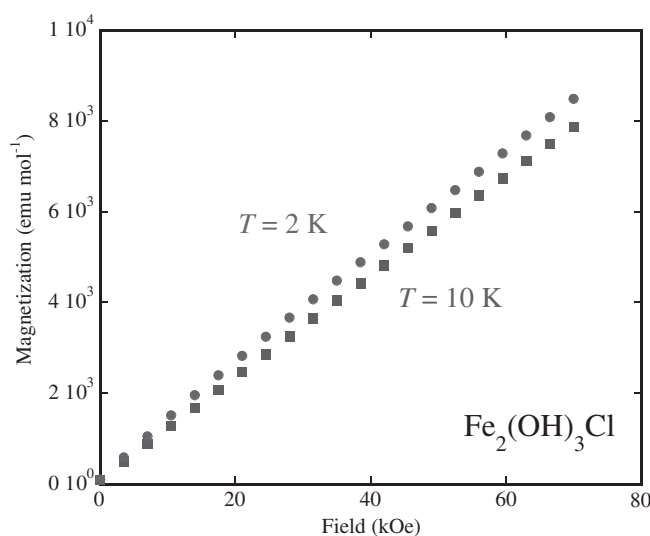
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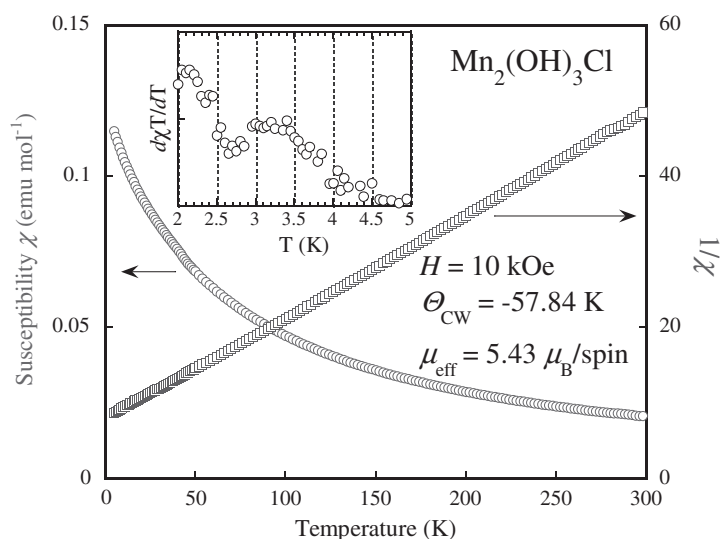**Figure 3.** Field dependence of the magnetization M–H at 2 and 10 K, respectively, for $Fe_2(OH)_3Cl$.

Figure 4. Temperature dependence of magnetic susceptibility $\chi \equiv M/H$ and its reciprocal at $H = 10$ kOe upon field cooling for $Mn_2(OH)_3Cl$. The inset is a $d(\chi T)/dT$–T plot to show small anomalies on the susceptibility curves.

Figure 4 shows the temperature dependences of χ and $1/\chi$ for $Mn_2(OH)_3Cl$. The susceptibility obeys the Curie–Weiss law with a paramagnetic Curie temperature (Θ_{CW}) of -57.8 K. An effective magnetic moment of 5.42 μ_B per Mn^{2+} spin was estimated from the susceptibility. This value is slightly smaller than the expected value of free Mn^{2+} ion, which we suppose to be a result influenced by the crystal field. The ZFC and FC magnetization curves in figure 5 indicate glassiness below 2.7 K. As shown in the inset plot in figure 4 (temperature differential of χT), two anomalies around 2.7 and 3.3 K are seen.
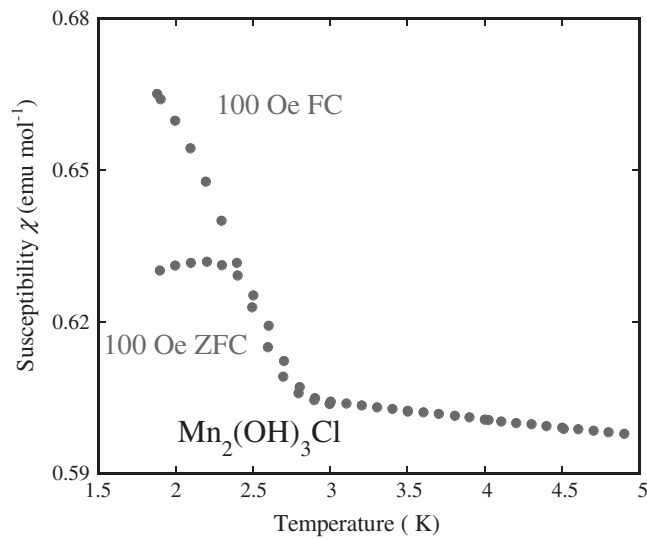
Figure 5. Temperature dependence of the susceptibility at 100 Oe under ZFC and FC conditions for $Mn_2(OH)_3Cl$.

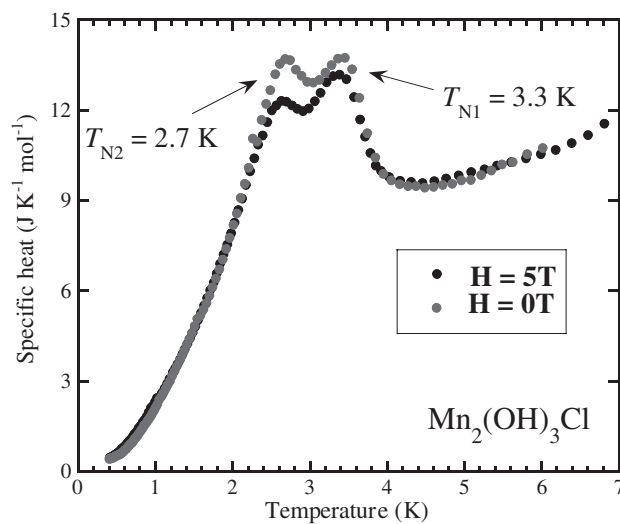**Figure 6.** Temperature dependence of the specific heat for $Mn_2(OH)_3Cl$ showing two successive phase transitions at 3.4 and 2.7 K, respectively.

In our previously reported clinoatacamite $Cu_2(OH)_3Cl$, a similar anomaly in $d(\chi T)/dT$ was recognized at $T_{N1} = 18.1$ K [4]. The specific heat measurement for $Mn_2(OH)_3Cl$ showed two successive phase transitions at 3.4 and 2.7 K, respectively (figure 6). The two peak positions slightly decrease in applied magnetic field, agreeing with its antiferromagnetic nature. The $M–H$ characteristics in figure 7 suggest that the ground states are antiferromagnetic. Therefore, we conclude that there are two successive antiferromagnetic transitions at $T_{N1} = 3.4$ K and $T_{N2} = 2.7$ K, respectively, for $Mn_2(OH)_3Cl$. The appearance of glassiness below the second antiferromagnetic transition resembles that in clinoatacamite $Cu_2(OH)_3Cl$ [4].

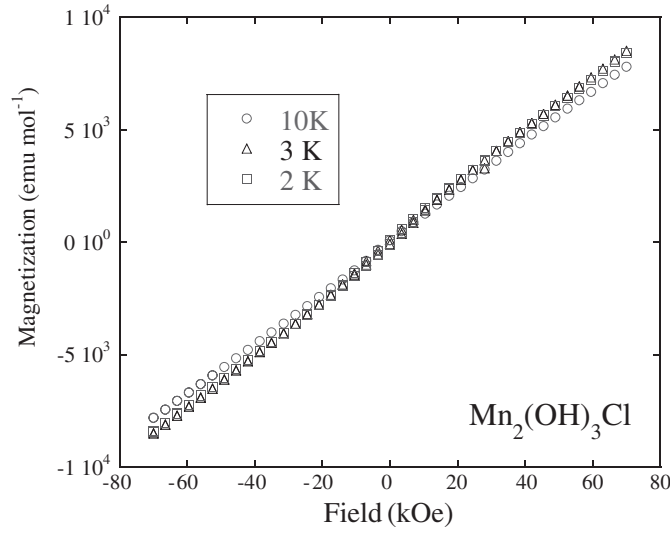**Figure 7.** Field dependence of the magnetization $M-H$ at typical temperatures for $Mn_2(OH)_3Cl$.

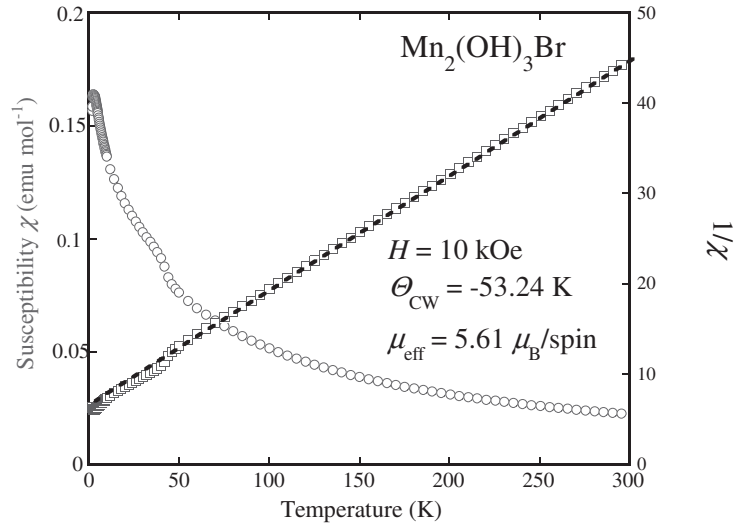**Figure 8.** Temperature dependence of magnetic susceptibility $\chi \equiv M/H$ and its reciprocal at $H = 10$ kOe upon field cooling for $Mn_2(OH)_3Br$.

The susceptibility results for $Mn_2(OH)_3Br$ are shown in figures 8 and 9. A paramagnetic Curie temperature of $\Theta_{CW} = -53.2$ K was obtained with an effective moment of $\mu_{eff} = 5.61 \mu_B$/spin (the small value is supposed to be due to the crystal field similar to $Mn_2(OH)_3Cl$). The small anomaly near 40 K was due to the inclusion of a small quantity of Mn_3O_4 that shows ferromagnetic behaviour below 42 K. We confirmed by x-ray diffraction that when the sample of $Mn_2(OH)_3Br$ was exposed to air for a long time the impurity phase of Mn_3O_4 appeared and the anomaly in susceptibility around 40 K grew larger. For both $Mn_2(OH)_3Cl$ and $Mn_2(OH)_3Br$, the Θ_{CW} are much higher than the T_N, suggesting magnetic frustration for both compounds. $Mn_2(OH)_3Br$ showed similar successive antiferromagnetic transitions

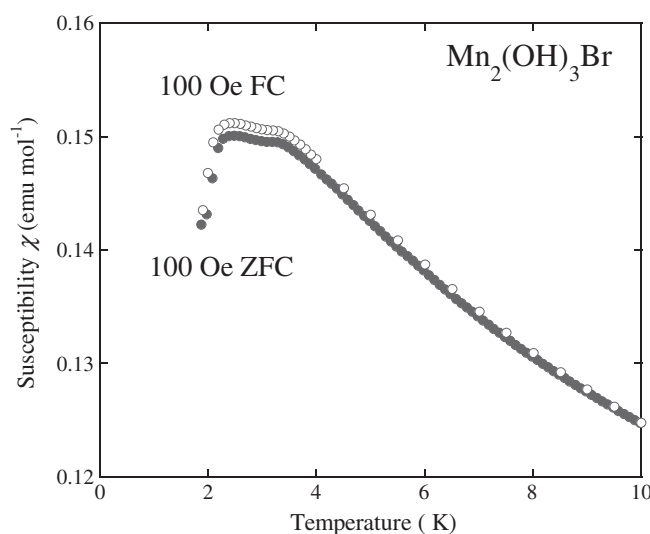**Figure 9.** Temperature dependence of the susceptibility at 100 Oe under ZFC and FC conditions for $Mn_2(OH)_3Br$.

as $Mn_2(OH)_3Cl$ with $T_{N1} = 3.3$ K and $T_{N2} = 2.4$ K, respectively. However, $Mn_2(OH)_3Br$ did not show a coexisting glassiness. The contrasting behaviours in $Mn_2(OH)_3Cl$ and $Mn_2(OH)_3Br$ are of great interest. Both compounds feature a slightly distorted tetrahedral lattice including the magnetic ions. The magnetic ions can be viewed as the alternative stacking layers of triangular lattice planes and Kagome lattice planes, with the magnetic ions on the Kagome lattice planes being bonded by the halogen ions. The contrasting behaviours in $Mn_2(OH)_3Cl$ and $Mn_2(OH)_3Br$ suggest that the glassiness arises from competing magnetic interactions on the Kagome lattice planes. The susceptibility behaviours in $Mn_2(OH)_3Cl$ strikingly resemble those of clinoatacamite $Cu_2(OH)_3Cl$, where a long-range antiferromagnetic order develops at $T_{N1} = 18.1$ K and then a coexisting state of long-range order and spin fluctuation prevails below $T_{N2} = 16.4$ K together with spin-glass-like behaviours [4, 5]. It is amazing that $Mn_2(OH)_3Br$ shows nearly the same transition temperatures but without the glassiness. Further experiments using μSR and neutron diffraction are in progress to reveal the differences between these two compounds.

The temperature dependence curves of χ and $1/\chi$ for $Co_2(OH)_3Br$ are presented in figure 10. A Θ_{CW} around -3 K and a μ_{eff} of 4.87 μ_B/spin are obtained. An antiferromagnetic transition was recognized directly on the χ–T curve at $T_N = 5$ K. No frustration was seen from these behaviours. These behaviours can be consistently explained by assuming a long range antiferromagnetic order with spins on the four corners of the tetrahedron pointing to the centre of the tetrahedron (i.e. the all-in all-out structure).

4. Conclusion

In summary, we have found a new geometric frustration material series $M_2(OH)_3X$ for d-electron magnetic ions on tetrahedral lattices. A systematic magnetic study has revealed for the first time antiferromagnetic transitions for these transition metal hydroxyhalides, i.e. $T_N = 14$ K for $Fe_2(OH)_3Cl$, successive transitions with $T_{N1} = 3.4$ K and $T_{N2} = 2.7$ K for $Mn_2(OH)_3Cl$, $T_{N1} = 3.3$ K and $T_{N2} = 2.4$ K for $Mn_2(OH)_3Br$, and $T_N = 5$ K for $Co_2(OH)_3Br$, respectively.
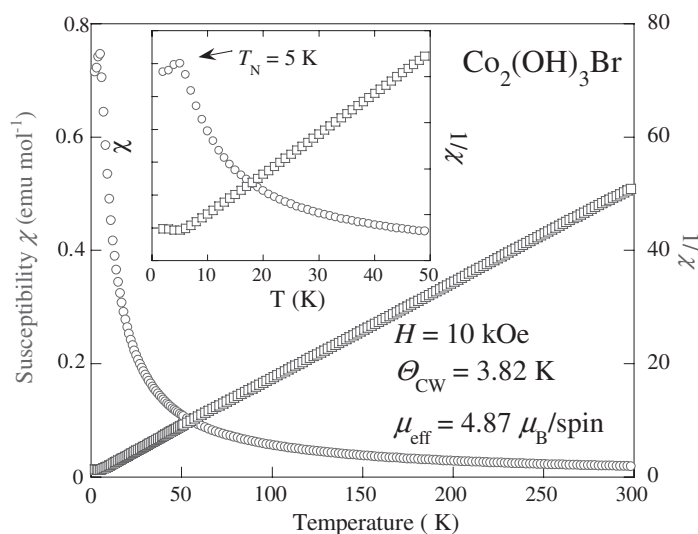
Figure 10. Temperature dependence of the magnetic susceptibility $\chi \equiv M/H$ and its reciprocal at $H = 1$ kOe upon field cooling for $Co_2(OH)_3Br$. The inset is an enlarged plot showing antiferromagnetic transition around $T_N = 5$ K.

While a long-range order is suggested for $Co_2(OH)_3Br$, strong geometric frustration is evidenced in $Fe_2(OH)_3Cl$, $Mn_2(OH)_3Cl$ and $Mn_2(OH)_3Br$. Furthermore, glassiness has been observed to coexist with the antiferromagnetism in the hydroxychloride compounds and the glassiness is shown to arise from competing magnetic interactions on the Kagome lattice planes. Further experiments using μSR and neutron diffraction are in progress to reveal their magnetic structures and the origin for the contrasting behaviours in this new geometric frustration series.

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