Magnetic Transitions in Botallackite-Structure Cu$_2$(OH)$_3$Br and Cu$_2$(OH)$_3$I

* X. G. Zheng$^{a,b}$, T. Yamashita$^b$, M. Hagihala$^b$, M. Fujihala$^b$, and T. Kawae$^c$

$^a$ Department of Physics, Faculty of Science and Engineering, Saga University, Saga 840-8502, Japan.
$^b$ Department of Physics, School of Engineering, Saga University, Saga 840-8502, Japan
$^c$ Department of Applied Quantum Physics, Faculty of Engineering, Kyushu University, Fukuoka 812-8581, Japan

Abstract

The deformed pyrochlore lattice compound clinoatacamite, Cu$_2$(OH)$_3$Cl, shows intriguing frustrated magnetism and 1/4 substitution of Cu with nonmagnetic Zn leads to the two-dimensional kagome lattice ZnCu$_3$Cl$_2$(OH)$_6$ that exhibits spin liquid behavior. These findings renewed interest in botallackite Cu$_2$(OH)$_3$Cl, which is a polymorphous structure of clinoatacamite Cu$_2$(OH)$_3$Cl possessing a two-dimensional triangular lattice. The present work investigates the effect of halogen ions on the magnetic transitions in the botallackite-structure. Similar to the antiferromagnetic Cu$_2$(OH)$_3$Cl ($T_N = 7.2$ K), Cu$_2$(OH)$_3$Br and Cu$_2$(OH)$_3$I both showed antiferromagnetic transitions at $T_N = 10$ K and 14 K, respectively. Long range order also exists in Cu$_2$(OH)$_3$Br as exemplified by the µSR study. The experimental results suggest that the magnetic coupling on the triangular lattice is dominated by the super-exchange interaction through the halogen ions. Further detailed comparison studies on these botallackite structure compounds are expected to clarify the spin configuration on this triangular lattice.

© 2001 Elsevier Science. All rights reserved

Keywords: Triangular lattice; Botallackite Cu$_2$(OH)$_3$Cl, Cu$_2$(OH)$_3$Br and Cu$_2$(OH)$_3$I.

1. Introduction

Geometrically frustrated magnetic materials for spins on triangular lattice, kagome lattice and tetrahedral lattice have been of intense recent interest due to the diversity in the exotic ground states that they display. 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].

The Cu$_2$(OH)$_3$Cl also has a polymorphous structure of a two-dimensional triangular lattice in botallackite. Apparently this triangular lattice for the $S = 1/2$ (Cu$^{2+}$) quantum spin is a good reference system for the tetrahedral lattice clinoatacamite Cu$_2$(OH)$_3$Cl and the kagome lattice ZnCu$_3$Cl$_2$(OH)$_6$. Botallackite also has a practical merit that benefits theoretical modelling because of the simplicity of the triangular configuration.

Our previous magnetization and µSR measurements revealed a long-range antiferromagnetic transition below $T_N = 7.2$ K for botallackite Cu$_2$(OH)$_3$Cl [4]. The present work further investigates the magnetic transitions in botallackite-structure Cu$_2$(OH)$_3$Br and Cu$_2$(OH)$_3$I. We hope the obtained information should help us to
understand the magnetic structure and the role of super exchange interactions, in special those through the OH and halogen bonding, as well as the effect of slight modification of the dimensionality in this triangular lattice. Our recent study on the tetrahedral lattice hydroxide halogenide $M_2(OH)_3X$ ($M$: transition metal, $X$: halogen ions) suggested that the halogen ions have a critical role on the magnetic frustration (5, 6).

2. Experimental

Polycrystalline samples were prepared by hydrothermal reaction of appropriate quantity of CuBr or CuI 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 (Japan). The magnetization was measured using a commercial SQUID magnetometer (MPMS-7). Muon spin rotation/relaxation ($\mu$SR) measurements were carried out at M20 at TRIUMF (Canada). Zero-field $\mu$SR were performed in a very weak field calibrated to less than 1 mOe.

3. Results and discussion

The as-prepared samples of Cu$_2$(OH)$_3$Br and Cu$_2$(OH)$_3$I were confirmed to be the botallackite phase in monoclinic, space group $P2_1/m$ (no. 11). The unit cell parameters are $a = 6.066(7)$ Å, $b = 6.142(7)$ Å and $c = 5.646(6)$ Å, $\beta = 93.58(1)°$ for Cu$_2$(OH)$_3$Br; $a = 6.5872(2)$ Å, $b = 6.1824(2)$ Å and $c = 5.6812(2)$ Å, $\beta = 95.060(2)°$ for Cu$_2$(OH)$_3$I. Compared with Cu$_2$(OH)$_3$Cl ($a = 5.7165$ Å, $b = 6.1182$ Å and $c = 5.6283$ Å, $\beta = 93.1161°$ as reported in ref. 4), the $a$-axis length, which is vertical to the two-dimensional triangular planes, is largely increased by replacing the relatively small Cl with larger ion radius Br and I.

As can be seen in the structure illustrated Fig. 1, the larger halogen ions strengthens the two-dimensionality, meanwhile the in-plane triangular lattice is not much influenced.

Figure 2 shows the temperature dependence of the magnetic susceptibility for the three compounds. Antiferromagnetic transitions at around $T_N = 7.2$ K, 10 K and 14 K, respectively were observed for Cu$_2$(OH)$_3$Cl, Cu$_2$(OH)$_3$Br and Cu$_2$(OH)$_3$I. They are featured by higher $T_N$ and lower peak value for larger halogen ions. The above experimental result strongly suggests that the magnetic coupling in these compounds is dominated by the super-exchange interaction through the halogen ions. This denies a simple expectation that the magnetic coupling in these structurally two-dimensional systems were dominated mainly by the much closer Cu-O-Cu bonding (refer to the structure in Fig. 2).
Fig. 2 The magnetic susceptibilities for botallackite-type \( \text{Cu}_2(\text{OH})_3\text{Cl} \), \( \text{Cu}_2(\text{OH})_3\text{Br} \) and \( \text{Cu}_2(\text{OH})_3\text{I} \) measured in field cooling at 1 Tesla.

The above tendency with the halogen ions also appeared in the \( M-H \) magnetization below \( T_N \) as shown in Fig. 3. All three compounds of \( \text{Cu}_2(\text{OH})_3\text{Cl} \), \( \text{Cu}_2(\text{OH})_3\text{Br} \) and \( \text{Cu}_2(\text{OH})_3\text{I} \) showed meta magnetism, i.e., the beginning of spin flop, at low fields. The field required for the occurring of the spin flop increased in the sequence of \( \text{Cu}_2(\text{OH})_3\text{Cl} < \text{Cu}_2(\text{OH})_3\text{Br} < \text{Cu}_2(\text{OH})_3\text{I} \), which is in consistency with their higher \( T_N \) values and hence stronger magnetic interaction for larger halogen ions. This property of the meta magnetism at low fields seems to reflect the instability of the antiferromagnetic spin structure on this two-dimensional triangular lattice.

The \( \mu \text{SR} \) measurement witnessed the development of a long range order for the \( \text{Cu}_2(\text{OH})_3\text{Br} \) below \( T_N = 10 \text{ K} \) (Fig. 4). The spectra of asymmetry for \( T > T_N \) are well fitted by the Kubo-Toyabe function,

\[
a(t) = a_0 \left[ \frac{1}{2} + \frac{2}{3} \left( 1 - \sigma^2 t^2 \right) \exp \left( -\frac{1}{2} \sigma^2 t^2 \right) \right],
\]

wherein the \( \sigma = 0.44 \text{ \mu s}^{-1} \), which is equivalent to the value previously observed for botallackite \( \text{Cu}_2(\text{OH})_3\text{Cl} \) and \( \text{Cu}_2(\text{OH})_3\text{I} \)\([4, 7]\). This fact suggests that muon stops around hydroxyl ion rather than halide ion in this system to produce the waterlike molecule: \( \mu^+ + \text{OH}^- = \text{MuOH} \). Thus muon serves as a probe for the local field that is produced by electron spin at oxygen site.

Fig. 3 The magnetization curves for botallackite-type \( \text{Cu}_2(\text{OH})_3\text{Cl} \), \( \text{Cu}_2(\text{OH})_3\text{Br} \) and \( \text{Cu}_2(\text{OH})_3\text{I} \), respectively, measured at 2 K.

Fig. 4 Zero-field \( \mu \text{SR} \) spectra for botallackite-structure \( \text{Cu}_2(\text{OH})_3\text{Br} \). The solid line represents the Kubo-Toyabe function fitting with \( \sigma = 0.44 \text{ \mu s}^{-1} \).
Fig. 5 Part of the short time spectra for botallackite-structure Cu$_2$(OH)$_3$Br at $T < T_N$.

For $T < T_N$, muon spin rotation was observed with distinct rotations as seen in Fig. 5. The phase diagram by plotting the muon-spin rotation frequency to temperature in Fig. 6 agrees with the antiferromagnetic transition at $T_N = 10$ K as seen in the susceptibility.

Similar $\mu$SR measurement for botallackite-structure Cu$_2$(OH)$_3$I verified three muon spin precession signals as denoted in Fig. 6.

It is interesting to note that the muon precession in Cu$_2$(OH)$_3$Br has two frequencies of 9.0 MHz and 15.5 MHz at the lowest temperature, and the Cu$_2$(OH)$_3$Cl sample showed 8.7 MHz and 21.9 MHz [4]. The low frequency was nearly equivalent in the two compounds, meanwhile, the high frequency quite differed. This fact suggests that in the ordered state there are two kinds of muon stop sites, one near the hydroxyl ion and another one is strongly influenced by the halide ion. The decrease of the highest frequency with larger halogen ions was further confirmed in Cu$_2$(OH)$_3$I but the latter showed an additional low frequency near 6 MHz (Fig. 6). Further simulation study of the three materials Cu$_2$(OH)$_3$Cl, Cu$_2$(OH)$_3$Br and Cu$_2$(OH)$_3$I may enable us to establish the spin structures in this botallackite system.

In summary, the effect of halogen ions on the magnetic transitions in the botallackite-structure was investigated. Similar to the antiferromagnetic Cu$_2$(OH)$_3$Cl ($T_N = 7.2$ K), both of Cu$_2$(OH)$_3$Br and Cu$_2$(OH)$_3$I showed antiferromagnetic transitions at $T_N = 10$ K and 14 K, respectively. Long range order was observed in Cu$_2$(OH)$_3$Br and Cu$_2$(OH)$_3$I with muon precession frequencies of 15.5 MHz and 9.0 MHz for Cu$_2$(OH)$_3$Br, and 13 MHz, 10 MHz and 6 MHz for Cu$_2$(OH)$_3$I, respectively, at the lowest temperature. The experimental results suggest that the magnetic coupling on the triangular lattice is dominated by the super-exchange interaction through the inter-plane halogen ions. Further detailed comparison studies on these botallackite structure compounds are expected to clarify the spin configuration on this triangular lattice.

**References**