Magnetic properties of geometrically frustrated polymorphic crystals of Cu$_{4-x}$Mg$_x$(OH)$_6$Cl$_2$

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Abstract. Geometric frustration can suppress magnetic long-range order (LRO) in either ferromagnetic (FM) [1-3] or antiferromagnetic (AFM) systems with Kagomé structure. Crystals of Cu$_{4-x}$Mg$_x$(OH)$_6$Cl$_2$, magnesium-containing paratacamite and herbertsmithite (x < 1 and x ~ 1, R3m) and haydeeite (x ~ 1, P3m1), have been grown by the hydrothermal technique and characterized by single crystal X-ray diffraction. The 2D S =1/2 polymorphs can be classified into the two types of magnets based on the susceptibility at high temperature. Temperature and dc field-dependence of magnetization of the magnesium-containing phase are quite similar to those of isostructural single crystals of Cu$_{4-x}$Zn$_x$(OH)$_6$Cl$_2$ (R3m), zinc-containing paratacamite (or herbertsmithite). However, for haydeeite, though a ferromagnetic long range ordering at 20.6 K can be predicted by the Curie-Weiss law, the magnetic phase transition is absent until 4.3 K, indicating a high degree of frustration (|θ|/Tc ~ 5). Its ac frequency and dc field-dependence of spin freezing temperature are analogous to those of spin ice and/or spin glass.

Strong geometric frustration usually arises in systems where the spins occupy the sites of a Kagomé structure. An AFM nearest-neighbor (NN) exchange in these systems may lead to a spin liquid state or valance-bond-solid state. However a FM exchange with strong single-ion anisotropy (Ising model) is assumed to attribute to the spin ice ground state in pyrochlore oxides of M$_2$Ti$_2$O$_7$ (M = Dy or Ho) where the Kagomé plane is perpendicular to the <111> axes [1-3]. It is commonly believed that the most promising candidate for exhibiting spin liquid state is the 2D spin-1/2 Kagomé lattice because quantum fluctuations are particularly strong for low spin systems; in contrast, significant super-exchange and dipolar interaction of spins with large moments play an important role in spin ice magnets rather than quantum fluctuations. Studies on isostructural systems and polymorphs are essential for verifying this belief due to their comparable magnetic properties. The report here involves novel polymorphs of Cu$_{4-x}$Mg$_x$(OH)$_6$Cl$_2$. Though arrangements of Cu$^{2+}$cations in the 2D Kagomé nets of the polymorphs are quite similar, their magnetic properties are strikingly different.

Crystals of Cu$_{4-x}$Mg$_x$(OH)$_6$Cl$_2$ were grown under hydrothermal conditions [4]. As an analogue of the Zn-containing atacamite family, the Mg-containing family has four members. Clinatacamite Cu$_2$(OH)$_2$Cl is the x = 0 end compound of the family [5]. This parent phase with P2$_1$/n structure has a deformed Kagomé lattice of Cu$^{2+}$ (S = ½). Two ideal x = 1 end compounds exist as polymorphs. One is haydeeite [6], an isostructural mineral of kapellasite (P3m1). The crystal structure of haydeeite is based on brucite-like sheets parallel to (0001) built from edge-sharing angle-distorted Mg(OH)$_6$ octahedra. The sheets containing perfect Kagomé lattices of Cu$^{2+}$ are stacked directly on each other (…AAA… stacking). Unit-cell parameters of a haydeeite of Cu$_{12.85}$Mg$_{1.15}$(OH)$_6$Cl$_2$ at 100 K are a = b = 6.2605(7) Å and c = 5.7218(7) Å. Another ideal x =1 end member is an isostructural compound of herbertsmithite (R3m). An ideal compound of Cu$_2$Mg(OH)$_6$Cl$_2$ with R3m structure can be named Mg-containing herbertsmithite (called Mg-herbertsmithite for short) and has not been reported in mineralogy. Its higher symmetry structure is caused by the substitution Mg for all of Cu$^{2+}$ in the interlayer of the parent phase, clinatacamite. Unit-cell parameters of Mg-herbertsmithite, Cu$_{10.00}$Mg$_{9.96}$(OH)$_6$Cl$_2$, at T = 100 K are a = b = 6.8337(10) Å and c = 13.965(2) Å. If the cations in the interlayer are partially replaced by Mg$^{2+}$, Mg-paratacamite appears as the fourth
phase, an analogue of Zn-paratracamite (R₃m or R₃) [5]. This phase is a closely related to Mg-
herbertsmithite (x = 1) in structure and does not show significant changes in Kagomé lattice
parameters when the concentration of Mg varies [6]. It is known that, with increasing number of Mg
occupying the interlayer sites, LRO temperature of Mg-paratracamites is decreased. For this reason,
one of the samples used here for magnetic measurements is a collection of single crystals of Mg-
paratracamite (x = 0.31) with ~1 mm diameter-size. This sample has a LRO transition at 4.7 K which is
comparable with that of well-known antiferromagnets of clinotracamite and Zn-paratracamite. Another
sample is a collection of 0.1 mm diameter-sized crystals of Haydeeite, Cu₂₂₈₃Mg₁₅(OH)₄Cl₂. Idealized
structure of the partial unit-cell of the R₃m phase and P₃m₁ phase are shown in the inset of Figure 1.

A SQUID magnetometer (MPMS2, Quantum Design Inc) was used to measure the dc
magnetization, M, as well as the real part, M′, and imaginary part, M′″, of the ac magnetization, M′ac,
with a drive amplitude of ~0.3 mT. All of the samples were randomly oriented with the applied field.

The main panel of Figure 1 shows the temperature-dependence of inverse dc susceptibility 1/χ, where χ = M/H, of clinotracamite, Zn-paratracamite (x = 0.34), Mg-paratracamite (x = 0.31) and
haydeeite (x = 1.15) at an applied field of H = 20 mT. Absence of any temperature hysteresis above 20
K indicates a paramagnetic (PM) character for all of the samples at high temperatures. The Curie-
Weiss law, χ = C/(T - θ), is a suitable model for the data within the temperature range of 200 K - 340
K. Fitting a straight line to each set of data yields the Curie constant, C = 0.483 and 0.441
(cm³/K/mol.Cu) for the Mg-paratracamite and haydeeite. Typical g-factors of 2.27 and 2.17 for Cu²⁺ (S
= ½) in the two polymorphs can be determined respectively. The Curie-Weiss temperature, θ, of the
Mg-paratracamite (x = 0.31) is -187 K, indicating an AFM character. This value is nearly equal to that of
Zn-paratracamite (x = 0.34), θ = -220 K. However, in contrast with these paratracamites, haydeeite
would have a FM ground state below θ = 20.6 K. Absence of LRO phase and spin
freezing until a critical temperature Tc ~ 4.3 K indicates a high degree of frustration (|θ|/Tc ~ 5) for this
system. Surprisingly, theoretical calculation [7] and phenomenological analysis [8] cannot deduce a
FM NN interaction because the O-H distance and the Cu-O-Cu angle between two neighbor plaquettes
reported here are 0.827 Å and 104.92 º. Therefore, it is possible to attribute to the dipole-dipole interaction and nearest-neighbor (NNN) interaction and/or interaction along the
diagonal of the Kagomé lattice. This situation is probably the same as that in the spin ice materials of
pyrochlore oxides implying haydeeite is an excellent candidate for demonstrating a quantum 2D spin
ice [9], as long as single-ion anisotropy of Cu²⁺ (S = ½) is involved in the frustration.

To reveal a difference in the magnetization process between Mg-paratracamite and haydeeite, one
can define an effective Curie constant \( C^{\text{eff}} = \frac{d(1/\chi)}{dT} \). This parameter is independent of the demagnetization factor, \( D \), because of an intrinsic susceptibility \( \chi_{\text{int}} = \chi/(1-4\pi D\chi) \). Temperature dependences of \( C^{\text{eff}} \) for clinoatacamite, Mg-paratacamites, and haydeeite are presented in Figure 1-(b). A separation between the \( C^{\text{eff}}-T \) curves starts at \( \approx 200 \text{ K} \) and increases at lower temperatures. The \( C^{\text{eff}}-T \) curves below 8 K presented in inset of Figure 1-(b) show different profiles: multi-peaked for clinoatacamite, single-peaked for Mg-paratacamite, and monotonically decreasing for haydeeite. These differences become trivial at \( T < 4 \text{ K} \). However, as shown in Figure 2-(a), the \( M-T \) curve of haydeeite is flat below a well-defined freezing temperature, \( T_f = 4.3 \text{ K} \), implying that spins freeze out. It is extremely different from that of clinoatacamite and Mg-paratacamite where a typical PM-FM phase transition occurs.

ZFC (zero field cooling) and FC (field cooling) measurements are used to detect the irreversibility of the magnetization process. As shown in Figure 2-(a), upon cooling, the FC curves of Mg-paratacamite and clinoatacamite increase monotonically, but the ZFC curves have a maximum at temperatures below their individual Curie points. For haydeeite, the ZFC magnetization is only slightly smaller than that of FC at same temperatures. Such a tiny difference in magnetization is further detected by minor M-H loops at an isothermal condition and lower field of up to 10 mT. Two loops shown in inset of Figure 2-(b) were performed after a zero field cooling. As an evidence of blocking phenomenon, magnetization (relative change of magnetization, \( \Delta M/M \)) of haydeeite at a higher temperature, \( 3 \text{ K} \), has a larger (smaller) value as compared with that at a lower temperature, \( 1.8 \text{ K} \).

Hysteresis loops using Mg-paratacamite and haydeeite were measured at \( T = 2 \text{ K} \) and a field of up to 5 T. As shown in the main panel of Figure 2-(b), an average magnetic moment for each \( \text{Cu}^{2+} \) in the \( \text{R}3\text{m} \) phase at 5 T is only 0.16 \( \mu_B \). This value and the slope of \( M \) vs. \( H \) at high field are comparable with that of Zn-paratacamite (\( x = 0.34 \)) in the same conditions. The weak magnetism is caused by a canting spin configuration in these systems. In contrast, haydeeite is mostly saturated at a field of \( \approx 1 \text{ T} \) and has a saturation moment of \( \approx 1.0 \mu_B/\text{Cu}^{2+} \). It is worth noting that at high field, the crystals might re-orient their magnetic easy axes along the applied field direction during the saturation process.

Nevertheless here is no lattice of corner-sharing tetrahedron in the structure and no significant random disorder of \( \text{Cu}^{2+} \) in the single crystal, haydeeite display a time-dependent magnetization reminiscent of what is observed in spin ice materials and/or spin glasses. Main panels of Figure 3-(a) and (b) show temperature dependences of ac magnetization of Mg-paratacamite and haydeeite at zero field. A sharp decline of \( M'_{\text{ac}} \) (or \( M''_{\text{ac}} \)) for Mg-paratacamite at LRO state indicates that the spins’ dynamic response is slowed such that it cannot respond to the time-varying drive field, which implies

Figure 2. (Color online) (a) Temperature-dependence of dc magnetization for clinoatacamite Mg-paratacamite and haydeeite. (b) Hysteresis loops of Mg-paratacamite (♦ and ○) and haydeeite (▲ and ●) at \( T = 2 \text{ K} \). Insert: relative changes of magnetizations (▲ and ▼) drawn from hysteresis loops for haydeeite at temperatures of 3 K (○ and ●) and 1.8 K (□ and ■). The fields swept up to 10 mT.
that upon cooling the spins gradually become firmly locked. For haydeeite, the M′ ac-T curve shows a slight decline at temperatures below Tf, while the M″ ac-T curve has a multistep structure. Beside a steep increase of M″ ac at Tf, a broad peak at a higher temperature can be detected on the M″ ac-T curve. The frequency-dependence of the peak temperature shown in the insert of Figure 3-(b) is quite similar to that of spin glass and/or spin ice systems. When a dc magnetic field was applied, the broad peak was suppressed. However, another maximum of M′ ac (and M″ ac) near the Tf appeared. As shown in the insert of Figure 3-(a), the temperature at which the maximum appears increases with increasing field. The field-dependence of the peak temperature is in striking contrast with the AT line in spin glasses, where a magnetic field suppresses its freezing temperature [10]. It is not clear now whether the nature of the enhanced Tf here is same as that in the 3D spin ice system [4]. One of explanations for the observation is that the application of a field enhances a short range ordering (which decreases the spin degree of freedom), consequentially suppressing the ac magnetization for all temperatures below Tf through spin locking. This assumption is consistent with the observation of the magnetization process shown in Figure 2-(b).

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Figure 3. (Color online) Main panels of (a) and (b) show M′ ac-T and M″ ac-T curves for Mg-paratacamite and haydeeite at a zero field (~ 0.1 mT). Insert of (a): M′ ac-T curves at varied dc fields. Inset of (b): frequency-dependence of M″ ac at a zero field.

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