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 $\text{Cu}_3\text{Mg}(\text{OH})_6\text{Br}_2$

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# Antiferromagnetism in kagome $\alpha\text{-Cu}_3\text{Mg}(\text{OH})_6\text{Br}_2$

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The antiferromagnetism in  $\alpha\text{-Cu}_3\text{Mg}(\text{OH})_6\text{Br}_2$  was studied by magnetic-susceptibility, specific-heat and neutron-diffraction measurements. The crystal structure consists of  $\text{Cu}^{2+}$  kagome layers with  $\text{Mg}^{2+}$  ions occupying the centers of the hexagons, separated by  $\text{Br}^{1-}$  ions. The magnetic system orders antiferromagnetically at 5.4 K with the magnetic moments aligned ferromagnetically within the kagome planes. The ordered moment is  $0.94 \mu_B$ , suggesting little quantum and geometrical fluctuations. By comparing the magnetic and specific-heat properties with those of the haydeeite, we suggest that  $\alpha\text{-Cu}_3\text{Mg}(\text{OH})_6\text{Br}_2$  may be described by the two-dimensional spin-1/2 Heisenberg kagome model and is in the region of the ferromagnetic-order side of the phase diagram.

## I. INTRODUCTION

The two-dimensional (2D) spin-1/2 kagome model has been intensely studied in theories because its rich ground states<sup>1–16</sup>. For example, the  $S = 1/2$  Heisenberg antiferromagnetic kagome model (AFKM) can give rise to ferromagnetic (FM) order, different types of antiferromagnetic (AFM) orders and quantum spin liquids (QSLs)<sup>7</sup>. The AFKM may be realized in many minerals of the atacamite group with the molecular formula as  $\text{Cu}_3T(\text{OH})_6X_2$ , where  $T$  and  $X$  are the  $3d$  non-magnetic transition-metal (Zn, Mg) and the halogen elements (F, Cl, Br), respectively. The most well-known material is the herbertsmithite  $\text{Cu}_3\text{Zn}(\text{OH})_6\text{Cl}_2$ , which shows no magnetic order down to at least 30 mK and is suggested to be a QSL<sup>17–24</sup>. The structure of  $\gamma\text{-Cu}_3\text{Mg}(\text{OH})_6\text{Cl}_2$  is very similar to that of the herbertsmithite and may also host a QSL state<sup>25</sup>. Recently, new materials  $\text{Cu}_3\text{Zn}(\text{OH})_6\text{FBr}$  and  $\text{Cu}_3\text{Zn}(\text{OH})_6\text{FCl}$  with similar structure have been successfully synthesized and shown to possibly host the gapped  $Z_2$  QSL ground states<sup>26–29</sup>.

In the above materials, the kagome layers formed by  $\text{Cu}^{2+}$  ions are separated by non-magnetic Zn or Mg ions, which may be treated as diamagnetic dilution of the three-dimensional (3D) pyrochlore-like lattice. These non-magnetic ions can also occupy the center of the hexagons in the kagome layers, as found in kapellasite,  $\alpha\text{-Cu}_3\text{Zn}(\text{OH})_6\text{Cl}_2$ <sup>30</sup> and haydeeite,  $\alpha\text{-Cu}_3\text{Mg}(\text{OH})_6\text{Cl}_2$ <sup>31</sup>. In this structure, the coupling between the kagome layers is through the weak interlayer O-H-Cl bonding, which

should result in highly 2D magnetic properties. It had been suggested that the kapellasite may be a gapless spin liquid or noncoplanar coboc2-type AF order<sup>3,32</sup>, but later measurements found strong Cu/Zn site mixing that makes the AFKM inappropriate<sup>33</sup>. The haydeeite is a rare example of the FM order for kagome magnets with  $T_c$  at 4.2 K<sup>34</sup>. Measurements on the single-crystal haydeeite further revealed strong anisotropic behaviors between the in-plane and out-of-plane magnetic properties<sup>35</sup>. Although the magnetic structure has not been unambiguously solved, the ordered moment is less than  $0.2 \mu_B$ , suggesting strong quantum fluctuations. Therefore, the haydeeite may be in the proximity to the quantum phase transition between the Heisenberg kagome FM order and the Heisenberg cuboc2 AF order<sup>34</sup>.

The idea for the compound of  $\text{Cu}_3\text{Mg}(\text{OH})_6\text{Br}_2$  comes from the substitution of interlayer  $\text{Cu}^{2+}$  in the barlowite  $\text{Cu}_4(\text{OH})_6\text{FBr}$ , which has perfect  $\text{Cu}^{2+}$  kagome layers with  $\text{Cu}^{2+}$  ions between them and is antiferromagnetically ordered at about 15 K<sup>36–40</sup>. It has been theoretically suggested that  $\text{Zn}^{2+}$  or  $\text{Mg}^{2+}$  ions can replace the interlayer  $\text{Cu}^{2+}$  in barlowite and thus dilute the AF order to give rise to a QSL state as in herbertsmithite<sup>41,42</sup>. While this proposal has been shown to succeed in  $\text{Cu}_3\text{Zn}(\text{OH})_6\text{FBr}$ <sup>26–28,39,43</sup>, no Mg-substituted barlowite has been reported. In this paper, we follow the same route in synthesizing the Zn-substituted barlowite to grow Mg-substituted barlowite. However, the final product is  $\text{Cu}_3\text{Mg}(\text{OH})_6\text{Br}_2$  because  $\text{MgF}_2$  cannot be dissolved in water. Since it has the same crystal structure as kapellasite and haydeeite, we

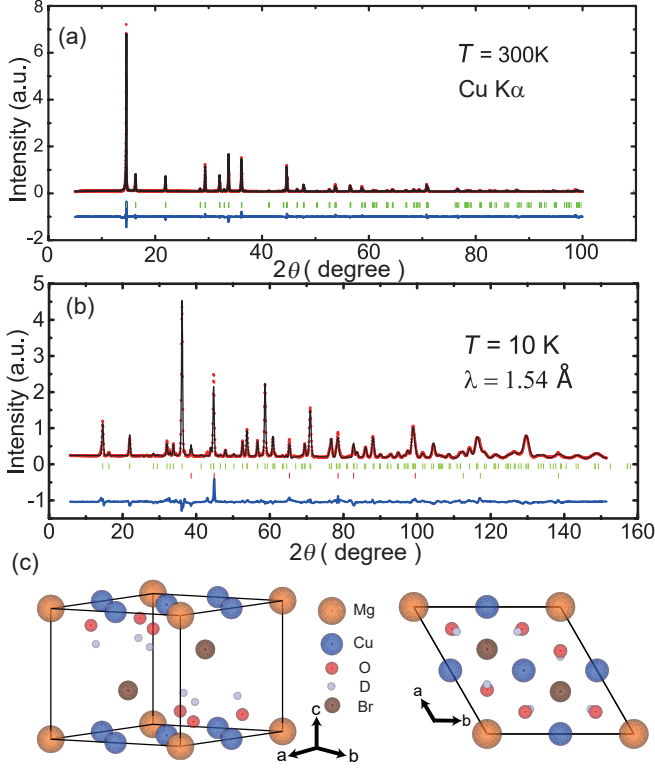


FIG. 1. (a) & (b) X-ray and Neutron powder diffraction intensities of  $\alpha$ -Cu<sub>3</sub>Mg(OD)<sub>6</sub>Br<sub>2</sub> (red dots) at 300 and 10 K, respectively. The calculated intensities are shown by the black lines. Short vertical green lines represents calculated Bragg peak positions. Vertical red lines represents Al peaks, which only exist in the neutron diffraction experiment due to the use of Al can. The blue lines show the differences between measured and calculated intensities. The weighted profile R-factor ( $R_{wp}$ ) at 300 and 10 K are 7.262 and 7.66%, respectively. Impurities are found in the neutron-scattering sample. These chemical impurities only exist in the deuterated sample. (c) Nuclear structure of  $\alpha$ -Cu<sub>3</sub>Mg(OD)<sub>6</sub>Br<sub>2</sub> (3D and top views).

Site	x	y	z	B (Å <sup>2</sup> )
Mg 1a	0.00000	0.00000	0.00000	0.281(406)
Cu 3e	0.50000	0.00000	0.00000	0.131(131)
Br 2d	0.33333	0.66667	0.63819(90)	0.117(155)
O 6i	0.82592(32)	0.17418(32)	-0.14100(64)	0.511(120)
D 6i	0.19300(41)	0.80700(41)	0.28666(98)	0.398(140)

TABLE I. Nuclear structure parameters of  $\alpha$ -Cu<sub>3</sub>Mg(OD)<sub>6</sub>Br<sub>2</sub> at 10 K.  $P\bar{3}m1$  (No. 164):  $a = b = 6.29314(20)$  Å,  $c = 6.10637(25)$  Å,  $\alpha = \beta = 90^\circ$ ,  $\gamma = 120^\circ$ .

label it as  $\alpha$ -Cu<sub>3</sub>Mg(OH)<sub>6</sub>Br<sub>2</sub>. The system orders anti-ferromagnetically at about 5.4 K but the configuration of the moments within the kagome plane is FM with the ordered moment of  $0.94 \mu_B$ . Our results suggest that  $\alpha$ -Cu<sub>3</sub>Mg(OH)<sub>6</sub>Br<sub>2</sub> is in the FM region of the phase diagram in the 2D Heisenberg kagome model.

## II. EXPERIMENTS

$\alpha$ -Cu<sub>3</sub>Mg(OH)<sub>6</sub>Br<sub>2</sub> was synthesized by the hydrothermal method as described previously<sup>26,39</sup>. The mixture of 1.5-mmol Cu<sub>2</sub>(OH)<sub>2</sub>CO<sub>3</sub> and 6-mmol MgBr<sub>2</sub>·6H<sub>2</sub>O was sealed in a 50-ml reaction vessel with 25-ml water, which was slowly heated to 200 °C and kept for 12 hours. The polycrystalline samples were obtained by washing the production with the deionized water. To produce deuterated samples, Cu<sub>2</sub>(OD)<sub>2</sub>CO<sub>3</sub> and heavy water were used in the above process. The Mg content is determined by the inductively coupled plasma mass spectrometer. The magnetic susceptibility and heat capacity were measured by the MPMS and PPMS (Quantum Design), respectively. The nuclear structure at room temperature was determined by powder x-ray diffraction (XRD) on Rigaku ultima IV X ray Diffractometer. The magnetic and nuclear structures at low temperatures were determined by neutron diffraction experiments performed on the HB-2A diffractometer at HFIR, USA, with the wavelengths of both 2.4103 and 1.5395 Å. The nuclear and magnetic structures are refined by the Fullprof program<sup>44</sup>.

## III. RESULTS AND DISCUSSIONS

Figure 1(a) and 1(b) show the powder diffraction results at 300 and 10 K by the XRD and neutron diffraction techniques, respectively. Refinements on these data give the same hexagonal nuclear structure with the space group of  $P\bar{3}m1$ , which suggests that there is no structural transition. Detailed refinement results at 10 K are shown in Table I. Since the coherent neutron scattering lengths of Cu and Mg are very different, their occupancies can be reliably refined. The values are 1.000(20) and 1.073(60) for Cu and Mg, respectively, if only one element is put onto 3e and 1a sites. On the other hand, one can only obtain very small negative occupancy value for either Cu at 1a or Mg at 3e site. Therefore, we conclude that there is no site mixing of Cu and Mg ions. Figure 1(c) gives the nuclear structure<sup>45</sup>. The Cu<sup>2+</sup> ions form kagome planes, which are separated by Br<sup>1-</sup> ions. The Mg<sup>2+</sup> ions sit at the centers of the hexagons within the Cu<sup>2+</sup> kagome planes.

At 1.6 K, the system becomes magnetically ordered as shown by the new peak in Fig. 2(a). The subtraction between 1.6 and 10 K data shows several magnetic peaks as shown in Fig. 2(b). The k-search method based on the first 3, 4 and 5 magnetic peaks all give a propagation vector  $k = (0, 0, 0.5)$ . Sarah program<sup>46,47</sup> was used to check the possible structures from the results of representational analysis based on the nuclear space group and magnetic propagation vector  $k$ . There are 3 irreducible representations (IRs),  $\Gamma_1$ ,  $\Gamma_3$  and  $\Gamma_5$ , which give the magnetic space groups as  $P\bar{3}m1$ ,  $P\bar{3}m'1$  and  $P1$ , respectively. These three IRs have 10 basis vectors (BVs)<sup>45</sup>, where  $\psi_6$  gives the best fitting results. The inset of Fig. 2(b) shows the magnetic structure. The moments at Cu<sup>2+</sup> positions

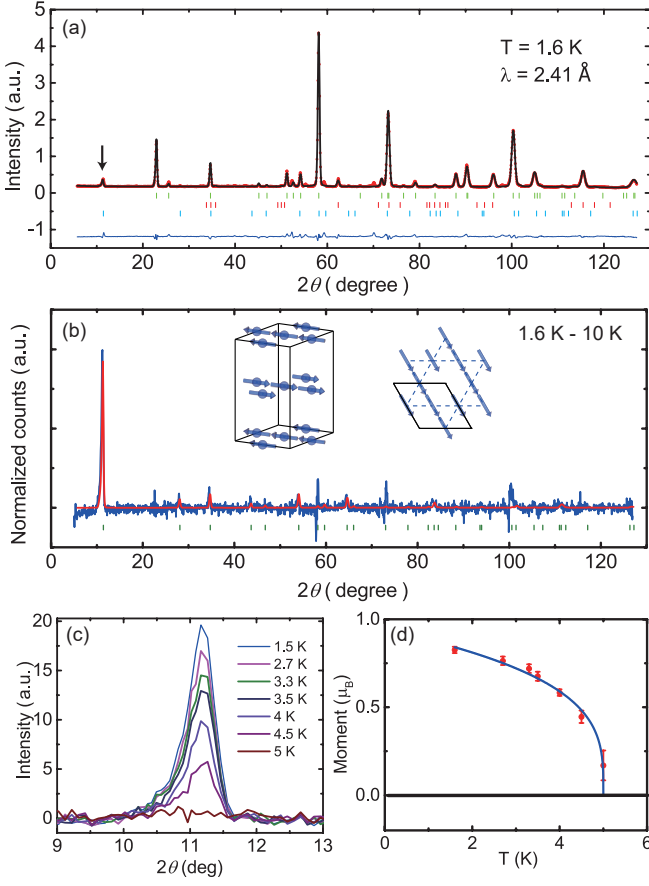


FIG. 2. (a) Neutron powder diffraction intensities of  $\alpha$ -Cu<sub>3</sub>Mg(OD)<sub>6</sub>Br<sub>2</sub> (red dots) at 1.6 K. The lines represent the same meanings as those in Fig. 1(a). The vertical blue lines represent magnetic peaks. The arrow shows the new peak appeared at this temperature. The weighted profile R-factor ( $R_{wp}$ ) is 14.1%. (b) The difference (blue lines) between the intensities at 1.6 K and 10 K for  $\alpha$ -Cu<sub>3</sub>Mg(OD)<sub>6</sub>Br<sub>2</sub>. The red lines represent the calculated intensities for the magnetic peaks. The vertical green lines represent magnetic peaks. The inset shows the magnetic structure. (c) The temperature dependence of the magnetic peak at (0, 0, 0.5). (d) The temperature dependence of the the moment. The error bars are from the refinements. The solid line is the fitted result as described in the main text with  $T_N$  fixed at 5 K, which is slightly different from that determined from the thermodynamical measurements as shown later, most likely due to the sample environment used in the neutron-diffraction experiment.

are confined within the kagome planes and ferromagnetically aligned along the b-axis. Along the c-axis, the moments are aligned antiferromagnetically.

Figure 2(c) shows the temperature dependence of the magnetic peak at (0, 0, 0.5) in the nuclear structural notation. Figure 2(d) shows the temperature dependence of the refined moment, which can be fitted by  $M_0(1 - T/T_N)^\beta$ . The values of  $M_0$  and  $\beta$  are  $0.94 \pm 0.03 \mu_B$  and  $0.29 \pm 0.03$ , respectively. The ordered moment  $M_0$  at 0 K is consistent with the ordered moment  $gS$  for a  $S$

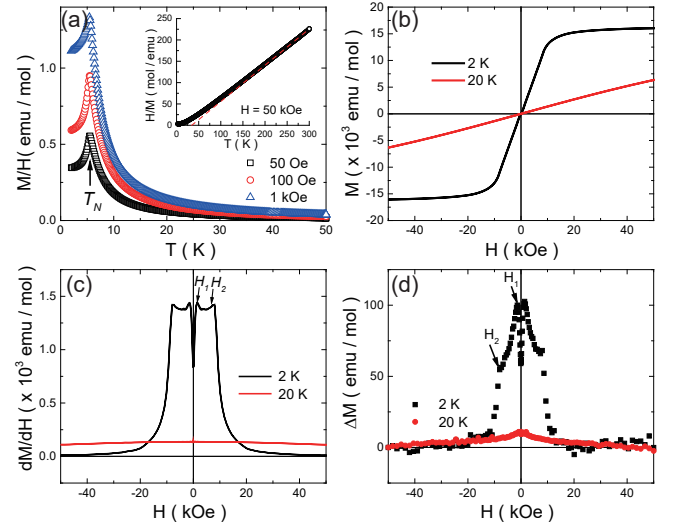


FIG. 3. (a) Temperature dependence of the  $M/H$  at 50 Oe, 100 Oe and 1 kOe. The arrow indicates the AF phase transition temperature. The inset shows the temperature dependence of  $H/M$  at 50 kOe. The dashed line is the linear fit to the high-temperature data. (b)  $M$ - $H$  loops at 2 and 20 K. (c)  $dM/dH$  at 2 and 20 K. (d) The difference of  $M$  between increasing and decreasing fields at 2 and 20 K.

$= 1/2$  system with  $g = 2$ .

Figure 3(a) gives the temperature dependence of the  $M/H$ , which clearly shows an AF phase transition at  $T_N = 5.54$  K. No significant difference is found between the field-cooled and zero-field-cooled processes. Above  $T_N$ ,  $M/H$  still strongly depends on the magnetic field, which suggests the presence of 2D spin fluctuations. The inset shows the temperature dependence of  $H/M$  at 50 kOe, which is roughly equivalent to the inverse of the magnetic susceptibility. The fitting at high temperatures gives a Curie temperature  $\theta$  of about 34 K and an effective moment of  $1.77 \mu_B$ , which is close to the value for  $S = 1/2$  with  $g = 2$ , i.e.  $g\sqrt{S(S+1)} = 1.732 \mu_B$ . Figure 3(b) shows the field dependence of the magnetization  $M$ . At 2 K,  $M$  becomes saturate above 20 kOe with the saturated moment of  $0.95 \mu_B$ , which also suggests that the system is  $S = 1/2$ . By taking the first derivative, two features can be seen at  $H_1 \approx 1.4$  kOe and  $H_2 \approx 8$  kOe as shown in Fig. 3(c). The value of  $H_1$  is similar to the saturated field for field parallel to the kagome planes in haydeeite<sup>35</sup>, which suggests that the easy-axis is within the kagome plane. These two characteristic fields can also be seen by the hysteresis behavior as shown in Fig. 3(d).

Figure 4(a) shows the specific heat of  $\alpha$ -Cu<sub>3</sub>Mg(OH)<sub>6</sub>Br<sub>2</sub> at several magnetic fields. The AF transition results in a large peak, which becomes a broad hump above 3 T due to the suppression of the transition. The background of the specific heat can be estimated by fitting the data from 15 to 30 K with  $C = \alpha T^2 + \beta T^3$  as shown by the dashed line in Fig. 4(a). The fitted values for  $\alpha$  and  $\beta$  are 0.0265

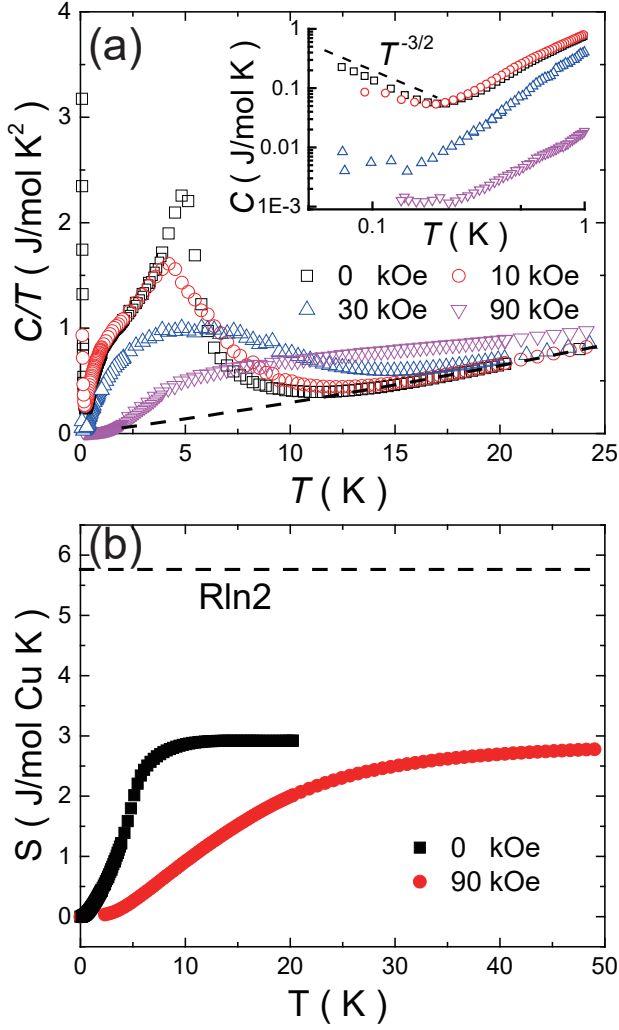


FIG. 4. (a) Temperature dependence of  $C/T$  at several fields. The black dashed line is the fitted result for the phonon contribution as discussed in the main text. The inset shows the specific heat  $C$  below 1 K. (b) Magnetic entropy associated with the magnetic transition at 0 and 90 kOe.

$\text{J/mol K}^3$  and  $2.86 \times 10^{-4} \text{ J/mol K}^4$ , respectively, similar to those in barlowite<sup>36</sup>. The cubic and square terms are from the contributions from phonons and 2D magnetic fluctuations, respectively. The Figure 4(b) shows the temperature dependence of the entropy released associated with the magnetic transition, which is obtained by the integration of  $C/T$  after subtracting the background as described above. The value of  $\Delta S_{AF}$  at high temperature is about  $3 \text{ J/mol Cu K}$ , which is just about half of  $R\ln 2$ . This is the typical behavior for quasi-2D spin systems, where spin correlations are formed well above  $T_N$ , as shown by the large value of  $\alpha$  and  $\theta$  in fitting the specific heat and magnetic susceptibility above  $T_N$ , respectively. It suggests that the magnetic couplings within the kagome planes should be much larger than that along the  $c$ -axis.

Interestingly, there is an upturn of  $C$  below 0.2 K as shown in the inset of Fig. 4(a), which can be fitted as  $C \propto T^{-3/2}$ . This kind of temperature dependence suggests that the upturn is not from the nuclear Schottky anomaly or magnetic impurities. Moreover, the specific heat should move to higher temperatures under fields if it comes from the nuclear Schottky anomaly or magnetic impurities. Instead, it is suppressed at 30 kOe and thus should be related to the intrinsic kagome system before the spins are fully polarized by the field. The entropy between 0.07 K to 0.2 K is about  $0.12 \text{ J/mol K}$ . It is not clear what is the origin of this upturn, but it is rather surprising since the system shows no exotic properties from other measurements.

Our results suggest that  $\alpha\text{-Cu}_3\text{Mg}(\text{OH})_6\text{Br}_2$  is another example for 2D Heisenberg kagome ferromagnetism. The antiferromagnetic alignment along the  $c$ -axis is due to the small interplane antiferromagnetic coupling. According to the 2D Heisenberg kagome model<sup>6,34</sup>, the magnetic interactions within a kagome plane mainly include nearest  $J_1$ , next-nearest  $J_2$ , next-next-nearest  $J_3$  and  $J'_3$ . For a ferromagnetic  $J_1 < 0$ , the system will show ferromagnetic order as far as  $J_2$ ,  $J_3$  and  $J'_3$  are negative or their absolute values are smaller than  $|J_1|$ . For haydeeite, it has been shown that its magnetic ground states may sit near the boundary between the FM and cuboc2 type noncoplanar AFM parts in the phase diagram since its ordered moment is just  $0.2 \mu_B$  due to strong quantum fluctuations<sup>34</sup>. In our case, the Curie-Weiss temperature from the magnetic-susceptibility measurement is 34 K, which is slightly larger than that in haydeeite (28 K)<sup>34</sup>. Considering that they have same nuclear and in-plane magnetic structures, it is reasonable to conclude that, for  $\alpha\text{-Cu}_3\text{Mg}(\text{OH})_6\text{Br}_2$ , the dominated magnetic interaction is also the ferromagnetic  $J_1$ . Because the ordered moment of our sample is  $0.94 \mu_B$ , the effect of quantum fluctuations should be much weaker. Therefore,  $\alpha\text{-Cu}_3\text{Mg}(\text{OH})_6\text{Br}_2$  is most likely in the FM part that is away from the boundary. It is also worth noting that while there are diluting effects of Mg on Cu sites for haydeeite, our sample shows no site mixing between Mg and Cu. While the large ordered moment makes  $\alpha\text{-Cu}_3\text{Mg}(\text{OH})_6\text{Br}_2$  less interesting due to the lack of frustration effects, it is worth noting that it may be another platform to study the topological bands in the kagome ferromagnet as observed in  $\text{Cu}[1,3\text{-benzenedicarboxylate}(\text{bdc})]^{48}$ .

#### IV. CONCLUSIONS

Our systematically studies on the magnetism in  $\alpha\text{-Cu}_3\text{Mg}(\text{OH})_6\text{Br}_2$  demonstrate that it orders antiferromagnetically below 5.54 K but the moments are aligned ferromagnetically within the kagome planes. The FM state of the kagome planes can be achieved easily by applying a weak magnetic field and its fluctuations survive above  $T_N$ . Our results suggest that  $\alpha\text{-Cu}_3\text{Mg}(\text{OH})_6\text{Br}_2$

is in the FM part in the phase diagram of 2D Heisenberg kagome model.

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