


**Engelhauptite: A variant of  $S = \frac{1}{2}$  kagome antiferromagnet**

Hajime Ishikawa, Daisuke Nishio-Hamane, Atsushi Miyake, Masashi Tokunaga, Akira Matsuo, Koichi Kindo, and Zenji Hiroi  
*Institute for Solid State Physics, the University of Tokyo, 5-1-5 Kashiwanoha, Kashiwa, Chiba, Japan*

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We have investigated the crystal structure and magnetic properties of the synthetic copper mineral engelhauptite,  $\text{KCu}_3\text{V}_2\text{O}_7(\text{OH})_2\text{Cl}$ , which possesses a kagome lattice made of  $\text{Cu}^{2+}$  ( $3d^9$ ) ions. Unlike the hexagonal structure with a perfect kagome lattice reported in the natural mineral, a synthetic crystal has a monoclinic structure with a distorted kagome lattice. We observe a magnetic transition at 6 K and an anomaly in the magnetization curve around 50 T. Engelhauptite represents a variant of the  $S = 1/2$  kagome antiferromagnet and we discuss the structure-property relationship by comparing engelhauptite and its relative compound volborthite,  $\text{Cu}_3\text{V}_2\text{O}_7(\text{OH})_2 \cdot 2\text{H}_2\text{O}$ .

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**I. INTRODUCTION**

Minerals with  $\text{Cu}^{2+}$  ( $3d^9$ ) ions materialize quantum spin systems with various lattice geometries [1]. Particularly interesting is the antiferromagnet with the two-dimensional kagome lattice made of corner-sharing triangles, where geometrical frustration is crucial. Theoretically, the  $S = 1/2$  kagome antiferromagnet is supposed to host spin-liquid ground states [2] and exhibit exotic magnetization plateaus in magnetic fields [3,4]. Experimentally, many copper minerals with kagome lattices have been investigated. For example, herbertsmithite,  $\text{ZnCu}_3(\text{OH})_6\text{Cl}_2$ , does not exhibit long-range magnetic order down to the lowest temperature measured and its ground state is considered as a spin liquid [5,6]. It is known that there is a crystallographic disorder caused by the mixing of nonmagnetic  $\text{Zn}^{2+}$  and magnetic  $\text{Cu}^{2+}$  ions owing to their similar ionic sizes. The relationship between the crystallographic disorder and the spin-liquid behavior is still under debate [7].

While a perfect  $S = 1/2$  kagome antiferromagnet without crystallographic disorder has still been sought, modified kagome antiferromagnets having deviations such as lattice distortions, extra interactions, and couplings with the lattice sometimes bring about unexpectedly interesting magnetism [8–10]. For example, volborthite,  $\text{Cu}_3\text{V}_2\text{O}_7(\text{OH})_2 \cdot 2\text{H}_2\text{O}$ , with a distorted kagome lattice exhibits a unique structural phase transition accompanied by a rearrangement of the spin-carrying Cu-3d orbitals around room temperature [8], which drastically modifies exchange interactions and its ground state [Fig. 1(a)]. Experiments using a single-crystal sample in strong magnetic fields have identified at least four different magnetic phases called phases I (below 4.5 T), II (4.5–26 T), N (26–28 T), and P (above 28 T) [11]. A plausible spin model for the low-temperature structure of volborthite is the “coupled-trimer model” proposed by Janson *et al.* [12], in which antiferromagnetically coupled linear trimers with strong intratrimer interactions are arranged to form a distorted square lattice on the underlying kagome net [Fig. 1(a)]. In this model, phase P, which is the  $1/3$  plateau phase, corresponds to the fully saturated state of the effective spin  $1/2$  in the

trimers. A condensation of bound-magnon pairs, which yields a spin nematic state, is proposed in phase N [12]. Recent heat capacity measurements reveal another phase called phase N2 between phases N and P; phase N2 may be a candidate for the spin nematic state [13]. On the other hand, curious magnetic anomalies called “magnetization steps” reported previously for the powder sample of volborthite at around 26 and 46 T [14] were not observed in the single-crystal sample.

Engelhauptite,  $\text{KCu}_3\text{V}_2\text{O}_7(\text{OH})_2\text{Cl}$ , is a candidate for the ideal  $S = 1/2$  kagome antiferromagnet [15], which has a similar chemical formula to volborthite,  $\text{Cu}_3\text{V}_2\text{O}_7(\text{OH})_2 \cdot 2\text{H}_2\text{O}$ . For a natural crystal, the hexagonal crystal structure with the space group  $P6_3/mmc$ , where the  $\text{Cu}^{2+}$  ions form a perfect kagome lattice, was reported. Crystallographic disorder caused by the mixing of different metal ions was not detected, which is due to the differences of valences and sizes between the  $\text{Cu}^{2+}$  and the other nonmagnetic ions. We have successfully synthesized a pure powder sample of engelhauptite and studied its crystal structure and magnetic properties. We show that synthetic engelhauptite has a monoclinic structure with the space group  $P2_1/m$ , in which the kagome lattice is heavily distorted as in the high-temperature structure of volborthite. Magnetic susceptibility reveals an antiferromagnetic Weiss temperature of 115 K and a magnetic transition around 6 K, which is evidenced by the heat capacity measurement. The magnetization curve of engelhauptite exhibits an anomaly around 50 T, which resembles the magnetization step reported in the powder sample of volborthite.

**II. EXPERIMENT**

$\text{CuO}$  (99.99%) and  $\text{V}_2\text{O}_5$  (99.99%) were mixed in the molar ratio of 3:1 with large excess of KCl (99%) and 10 ml of pure  $\text{H}_2\text{O}$  in a Teflon beaker of 45 ml volume. The beaker was heated at 200 °C for 24 h in a stainless steel hydrothermal autoclave. The thus-obtained solid product was homogenized in an agate mortar and reacted again with KCl and  $\text{H}_2\text{O}$  in the same condition. Chemical analysis for the obtained dark yellow powder by the ICP-AES experiment revealed a molar ratio of K:Cu:V = 1:2.93:2.02, which is close to the

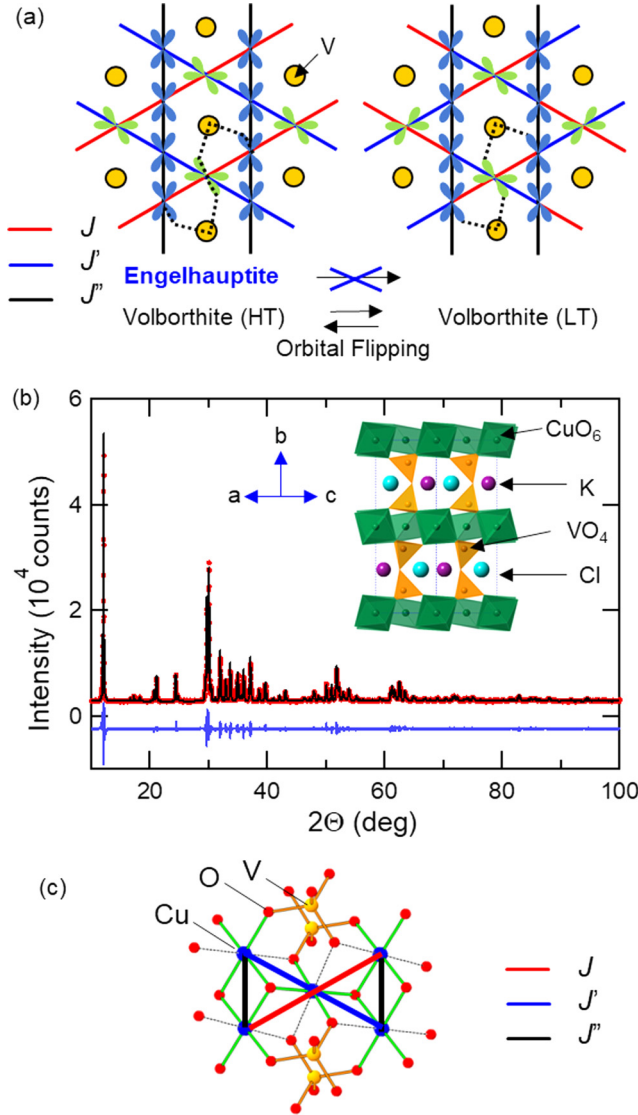


FIG. 1. (a) Arrangements of spin-carrying Cu-3d orbitals in the kagome layers in engelhauptite and the high-temperature  $C2/c$  structure of volborthite (left) and in the low-temperature structure of volborthite (right). The blue and green lobes indicate the  $d(x^2 - y^2)$ -type orbitals forming the chain and the orbitals between the chains, respectively. The yellow circles represent V ions above or below the kagome layer. The Cu-O-V-O-Cu superexchange path (black dotted line) is suggested to produce strong antiferromagnetic interactions (red lines) in Ref. [12]. (b) Powder x-ray diffraction pattern of synthetic engelhauptite. The observed intensity (red), calculated intensity (black), and their difference (blue) are shown. The crystal structure of engelhauptite viewed along the kagome layers is depicted in the inset. (c) The crystal structure commonly observed in engelhauptite and volborthite. The short (1.9–2.1 Å) and long (2.4–2.5 Å) Cu-O bonds are depicted by the thick green and black dashed lines, respectively. There are three kinds of nearest neighbor interactions  $J$  (red),  $J'$  (blue), and  $J''$  (black) between the Cu ions.

ideal stoichiometry of engelhauptite; the Cl content could not be analyzed in our apparatus. A powder x-ray diffraction pattern was obtained by a diffractometer with Cu  $K\alpha$  radiation. The powder pattern was analyzed by FULLPROF

TABLE I. Atomic coordinates of synthetic engelhauptite with monoclinic  $P2_1/m$  structure refined from the powder x-ray diffraction data, which has lattice constants  $a = 5.8622(1)$  Å,  $b = 14.5661(1)$  Å,  $c = 6.0770(1)$  Å,  $\beta = 119.062(1)^\circ$ .

Atom	$x$	$y$	$z$
K	0.173(3)	0.25	0.308(2)
Cu1	0.5	0	0.5
Cu2	0	0	0
Cu3	0	0	0.5
V	0.503(2)	0.1291(3)	0.962(1)
O1	0.805(4)	0.089(1)	0.111(4)
O2	0.352(3)	0.106(1)	0.132(4)
O3	0.329(5)	0.077(1)	0.663(4)
O4	0.836(5)	0.058(1)	0.674(3)
O5	0.524(4)	0.25	0.928(4)
Cl	0.842(2)	0.25	0.597(2)

software [16]. Magnetization and heat capacity measurements were performed by a commercial apparatus (Quantum Design MPMS3 and PPMS). Magnetization up to 70 T is measured by the induction method in the pulsed magnetic field at the International MegaGauss Science Laboratory in the Institute for Solid State Physics, the University of Tokyo.

### III. RESULTS

Figure 1(b) shows the powder x-ray diffraction pattern of synthetic engelhauptite. The powder pattern does not match with the hexagonal structure reported for a natural crystal. Instead, all the peaks are indexed by a monoclinic unit cell with the space group  $P2_1/m$  and lattice constants  $a = 5.8622(1)$  Å,  $b = 14.5661(1)$  Å,  $c = 6.0770(1)$  Å,  $\beta = 119.062(1)^\circ$ . We constructed an initial structural model so as to reproduce the hexagonal crystal structure of engelhauptite in the  $P2_1/m$  unit cell and refined the atomic positions by the Rietveld method. The powder pattern is perfectly reproduced by the crystal structure shown in the inset of Fig. 1(b) (see Table I for atomic coordinates). The crystal structure contains an edge-sharing network of  $\text{CuO}_6$  octahedra, where the Cu atoms form a distorted kagome lattice. There are three crystallographic Cu sites and three different Cu-Cu distances in the kagome lattice. Each Cu ion is surrounded by six oxygens with the 4-short-2-long-type coordination, where an unpaired electron occupies the “ $d(x^2 - y^2)$ -type” orbital extending toward the short Cu-O bonds [see Table II and Fig. 1(c)] [17]. Note the arrangement of the  $d(x^2 - y^2)$ -type orbitals in the kagome lattice is identical to that of the high-temperature structure of volborthite with the space group  $C2/c$  [18] [Fig. 1(a)].

The temperature dependence of the magnetic susceptibility,  $\chi(T)$ , of engelhauptite is shown in Fig. 2(a), which is compared with that of the single-crystal sample of volborthite.  $\chi(T)$  of engelhauptite exhibits Curie-Weiss behavior at high temperatures. A Curie-Weiss fit for the data above 200 K assuming  $\chi(T) = C/(T - \Theta)$ , where  $C$  and  $\Theta$  are the Curie constant and Weiss temperature, respectively, gives  $C = 0.497(2)$  ( $\text{cm}^3 \text{K mol}^{-1}$ ) and  $\Theta = -115(1)$  K. The  $C$  corresponds to the effective magnetic moment  $\mu_{\text{eff}} = 1.99 \mu_B/\text{Cu}$ , which is a typical value for  $\text{Cu}^{2+}$  ions and slightly larger than

TABLE II. Cu-O bond lengths in engelhauptite obtained from the powder x-ray diffraction data.

Bond	Length ( $\text{\AA}$ )
Cu1-O4	1.92(3)
Cu1-O3	2.05(3)
Cu1-O2	2.50(3)
Cu2-O4	1.92(2)
Cu2-O1	2.04(3)
Cu2-O2	2.38(2)
Cu3-O4	1.93(3)
Cu3-O3	2.03(3)
Cu3-O1	2.44(3)

$1.73 \mu_B$  expected for the pure  $S = 1/2$ . The large negative  $\Theta$  indicates dominant antiferromagnetic interactions. The  $\Theta$  of volborthite estimated from the Curie-Weiss fit above 290 K in the high-temperature form is  $-97(1)$  K. The  $\chi(T)$  of volborthite exhibits a clear kink with thermal hysteresis at the structural phase transition around 290 K. Such anomaly is not observed in engelhauptite [inset in Fig. 2(a)].

Around 20 K, the  $\chi(T)$  of engelhauptite exhibits a broad peak, which is often observed in the low-dimensional antiferromagnet. At 6 K, a kink is observed in the  $\chi(T)$  of engelhauptite suggesting a magnetic transition, which becomes obscured with increasing field [Fig. 2(b)]. The heat capacity divided by temperature,  $C_p(T)/T$ , exhibits a broad anomaly around 6 K, which evidences the bulk phase transition. The kink in the heat capacity is robust against magnetic field up to 7 T. Note that the divergence of  $\chi(T)$  toward low temperature or Schottky-type heat capacity, which are typical traces of orphan spins, is not observed. The broad feature may come from certain inhomogeneity in the sample, which is often the case for highly frustrated antiferromagnets; even tiny defects can affect the transition. Note that the transition temperature is much higher than in volborthite, which shows a magnetic transition around 1 K.

To explore possible magnetic field induced phases, the magnetization curve of engelhauptite is measured up to 70 T [Fig. 3(a)]. The magnetization increases monotonically up to 40 T and the slope becomes considerably smaller above 50 T, suggesting a certain magnetic phase transition. This magnetization process is completely different from that of the single-crystal sample of volborthite [Fig. 3(b)], which exhibits a steep increase around 26 T and a clear  $1/3$  magnetization plateau above 28 T, but rather like the magnetization step observed in the powder sample of volborthite at 46 T.

#### IV. DISCUSSION

Our synthetic sample of engelhauptite crystallizes in the monoclinic structure instead of the hexagonal structure reported for a natural mineral. In the hexagonal structure, the Cu ion has the 2-short-4-long-type coordination, which is quite rare for copper compounds. It has been pointed out that the hexagonal structure may be an artifact caused by the poor quality in crystals or in the diffraction data [15]. We consider that the hexagonal structure is obtained as a result of averaging over monoclinic  $P2_1/m$  domains or is associated with

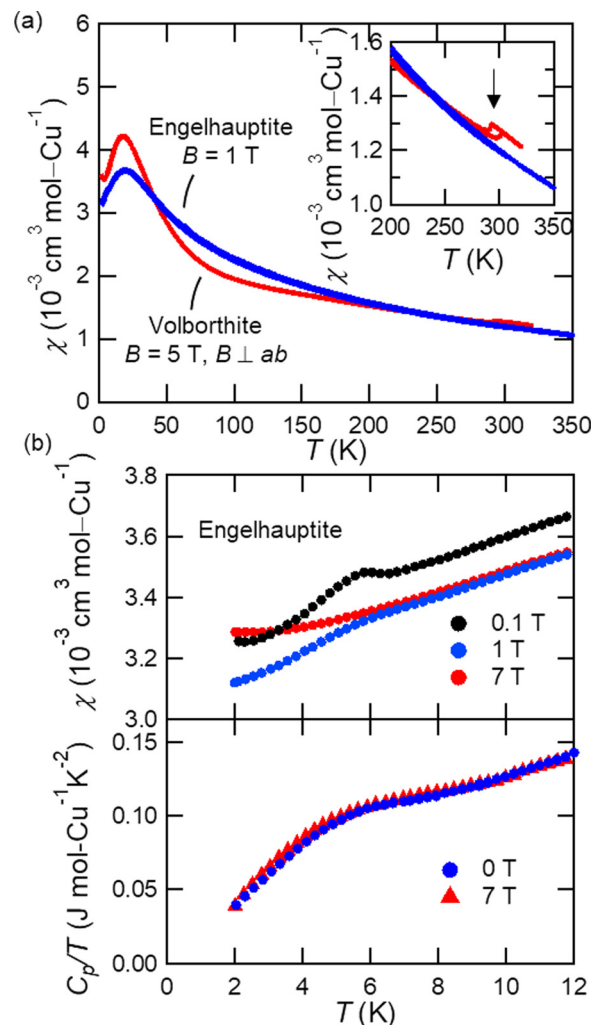


FIG. 2. (a) Temperature dependence of magnetic susceptibility  $\chi(T)$  of a powder of engelhauptite (blue) at 1 T and single crystals of volborthite (red) at 5 T in  $B \perp ab$ . (b)  $\chi(T)$  of engelhauptite measured at 0.1 (black), 1 (blue), and 7 (red) T with the zero-field cooling processes and the heat capacity divided by temperature  $C_p/T(T)$  of engelhauptite measured at 0 (blue) and 7 (red) T below 12 K.

microscopic disorder. This could be the case also for related mineral vesignieite,  $\text{BaCu}_3\text{V}_2\text{O}_8(\text{OH})_2$ ; a perfect kagome lattice made of  $\text{Cu}^{2+}$  ions with the 2-short-4-long-type coordination was reported previously, while another distorted crystal structure was proposed [19]. The 2-short-4-long type coordination is also observed in another polymorph of volborthite with the space group  $C2/m$  [8]. The  $C2/m$  structure of volborthite may be an averaged structure of  $C2/c$  domains with the 4-short-2-long-type coordination.

It is reasonable that engelhauptite and the high-temperature  $C2/c$  structure of volborthite have antiferromagnetic Weiss temperatures with similar magnitudes because they have identical orbital arrangements in the kagome layers. Volborthite has a different orbital arrangement below 290 K as shown in Fig. 1(a) as a result of the first-order structural phase transition called “orbital flipping” [20], which manifests in the magnetic susceptibility as shown in Fig. 2(a). The absence of such anomaly in engelhauptite can be attributed to the different

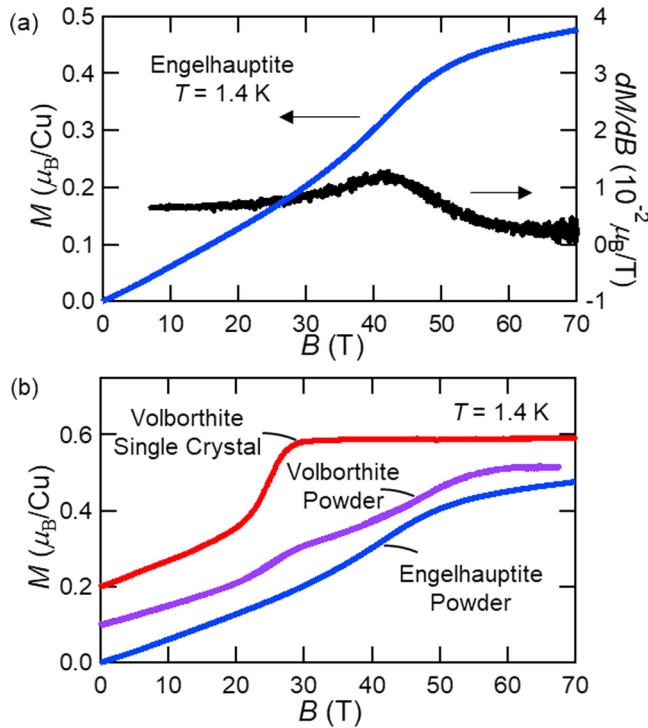


FIG. 3. (a) Magnetization curve of engelhauptite (blue) and its derivative by magnetic field (black) at 1.4 K in pulsed magnetic field. (b) Comparison of the magnetization curves between engelhauptite (blue) and volborthite in single crystal (red with offset of  $0.2 \mu_B$  in the vertical axis) and in powder (purple with offset of  $0.1 \mu_B$  in the vertical axis) [11,14]. All the measurements are performed at 1.4 K.

interlayer components. In the orbital-flipping transition of volborthite, not only the spin-carrying Cu-3d orbitals, but also the  $V_2O_7$  pillars and  $H_2O$  molecules between the layers change their arrangements simultaneously [8,18]. These cooperative motions may be driven by hydrogen bonding between the  $H_2O$  molecules and the oxygens constituting the  $CuO_6$  octahedra and the  $V_2O_7$  pillars [8]. In engelhauptite, in contrast, ionic bonding between layers via the  $K^+$  and  $Cl^-$  ions, which should be stronger than the hydrogen bonding, may not allow further structural changes.

The marked difference in the magnetization curves at low temperature between engelhauptite and volborthite in Fig. 3(b) should be ascribed to the different orbital patterns at low temperatures. The kagome layers of both compounds are made of nearly identical local structure shown in Fig. 1(c). There are three types of nearest-neighbor interactions, named

$J$ ,  $J'$  and  $J''$ . In engelhauptite and the high-temperature structure of volborthite, there are three kinds of chains made from one of the three interactions [red, blue, and black lines in Fig. 1(a)]. On the other hand, there are two kinds of chains, i.e., “ $J$ - $J'$ - $J'$  chain” and “ $J''$  chain”, in the low-temperature structure of volborthite [Fig. 1(a)]. The difference of the arrangement of  $J$  and  $J'$  comes from the arrangement of the  $d(x^2 - y^2)$ -type orbitals [green lobes in Fig. 1(a)] between the chains of other  $d(x^2 - y^2)$ -type orbitals [blue lobes in Fig. 1(a)]. They are arranged in phase in engelhauptite and the high-temperature structure of volborthite within the kagome plane, while are staggered in the low-temperature structure of volborthite as a result of the orbital-flipping transition. According to the theoretical study for volborthite [12],  $J$  is antiferromagnetic and much stronger than ferromagnetic  $J'$  and  $J''$  enhanced by the Cu-O-V-O-Cu superexchange path [black dashed lines in Fig. 1(a)]. The magnetization plateau at  $1/3$  of the saturation magnetization is understood as the saturation of the magnetic trimer coupled by  $J$  in the “ $J$ - $J'$ - $J'$  chain” in volborthite [12]. The absence of the  $1/3$  magnetization plateau in engelhauptite is reasonable because the  $J$  forms chains instead of the trimers.

Note that the magnetization steps at 26 and 46 T observed in the powder sample of volborthite appear to be reproduced by assuming two components which behave as the single crystal of volborthite and engelhauptite [Fig. 3(b)]. Indeed, the nuclear magnetic resonance spectra of the powder sample of volborthite are made of two components, one of which is absent in the single crystal [11]. A possible explanation of the unusual magnetization curve of the powder sample of volborthite is a disorder in the arrangement of  $d(x^2 - y^2)$ -type orbitals which flip in the orbital-flipping transition [green lobes in Fig. 1(a)]. Such disorder may allow the coexistence of trimers and engelhauptite-type component.

## V. CONCLUSION

We have synthesized the mineral engelhauptite and investigated its crystal structure and magnetic properties. It is shown that engelhauptite is a distorted  $S = 1/2$  kagome antiferromagnet, which exhibits a magnetic order at 6 K and a certain magnetic field induced transition at around 50 T. Engelhauptite has a unique arrangement of the 3d orbitals in the kagome net and is identical to that of the high-temperature form of volborthite. Clarifying the ground state at low- and high-field regions and the underlying magnetic interactions by neutron scattering experiments and theoretical investigations is interesting future work.

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