

Noncollinear spin order, field-induced transitions, and short-range correlations in $\text{Cu}_4\text{SO}_4(\text{OH})_6$

Oleksandr Prokhnenko¹, Koji Kaneko^{2,3}, Chihiro Tabata^{2,3}, Mitsuru Akaki⁴, Chanhyeon Lee⁴, Takayoshi Yamanaka⁴, Hironori Sakai³, Yusuke Hirose^{2,3}, Alsu Gazizulina¹, Yoshifumi Tokiwa³, Yoshinori Haga³, Motoi Kimata³, Masaki Fujita⁴, Hiroyuki Nojiri⁴, Lawrence M. Anovitz⁵, and Andrey Podlesnyak⁶

¹*Helmholtz-Zentrum Berlin für Materialien und Energie, Hahn-Meitner-Platz 1, D-14109 Berlin, Germany*

²*Materials Sciences Research Center, Japan Atomic Energy Agency, Tokai, Ibaraki 319-1195, Japan*

³*Advanced Science Research Center, Japan Atomic Energy Agency, Tokai, Ibaraki 319-1195, Japan*

⁴*Institute for Materials Research, Tohoku University, Sendai 980-8577, Japan*

⁵*Chemical Sciences Division, Oak Ridge National Laboratory, Oak Ridge, Tennessee 37831, USA*

⁶*Neutron Scattering Division, Oak Ridge National Laboratory, Oak Ridge, Tennessee 37831, USA*



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We report a comprehensive study of spin- $\frac{1}{2}$ quantum magnet brochantite, $\text{Cu}_4\text{SO}_4(\text{OH})_6$, combining high-field thermodynamic measurements, polarized neutron diffraction, inelastic neutron scattering, and nuclear magnetic resonance spectroscopy. Using bulk magnetization and specific heat measurements we construct the magnetic H - T phase diagram for magnetic fields applied along main crystallographic directions up to 24.1 T. Polarized neutron diffraction reveals a noncollinear magnetic ground state confined to the ab plane. A field-induced transition is observed for magnetic fields in the ab plane whose critical field and character evolve continuously with field direction in the ab plane. While the transition for $H \parallel b$ might be a spin-flop-like transition, the one for $H \parallel a$ resembles the short-range correlated state above T_N , suggesting a magnetic configuration related to the quasi-two-dimensional correlations in the bc planes. The experimental results demonstrate that the ground-state and field-induced phases cannot be explained by a simple XXZ model with a single dominant exchange interaction and that weaker interchain and anisotropic interactions have to be taken into account. Our work establishes brochantite as a low-symmetry Cu-based quantum magnet with noncollinear order and complex field-induced behavior.

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I. INTRODUCTION

Magnetic systems comprising spin- $\frac{1}{2}$ ions have been in a focus of condensed matter physics for several decades. Being subject to enhanced spin fluctuations often combined with reduced dimensionality and/or magnetic frustration, these materials create a rich landscape for exotic physical phenomena. These include quantum spin liquids and fractional excitations, Bose-Einstein condensation and dimerization, magnetization plateaus, and Kitaev physics amongst others (see, e.g. [1–8], and references therein). Beyond their fundamental interest, these materials have significant practical importance, particularly in connection with magnonics, which is based on collective motions of magnetic moments instead of mobile charges, or quantum information, where such systems can be used as quantum simulators or qubits [9–15].

Significant progress in understanding these materials has been achieved by improvements in both theory and numerical methods, and advances in solid state chemistry and measurement techniques. Among the latter the ability to produce the large, high-quality single crystals necessary to perform

neutron scattering (NS) experiments has been critical. NS provides direct access to static and dynamic correlations in matter with great detail, but despite advances in neutron sources and instrumentation, still requires relatively large samples given the weak interaction cross section of neutrons with matter. Because of this, there are still cases where nature outperforms human capabilities in the preparation of suitable samples. For example, until now the spin- $\frac{1}{2}$ compound $\text{Cu}_4\text{SO}_4(\text{OH})_6$, known as the mineral brochantite, could only be produced in powder form or as tiny crystals [16,17]. In contrast, natural minerals found in several places around the globe can readily reach 1 cm³ or more. Brochantite is a common corrosion product on bronze sculptures, giving rise to green patina during outdoor weathering of, e.g., the Statue of Liberty. Other reasons, however, have recently stimulated interest in this compound. One is the search for quantum spin-liquid candidates, which has pointed to $\text{Cu}_4\text{SO}_4(\text{OH})_6$ and $\text{ZnCu}_3(\text{OH})_6\text{SO}_4$ (so called Zn-brochantite) as geometrically frustrated, two-dimensional Heisenberg quantum kagome antiferromagnets [16,18–20]. The other is nonreciprocal magnons, which have different energies for wave vectors of equal length and opposite direction due to the antisymmetric Dzyaloshinskii-Moriya interaction (DMI). This phenomenon opens the possibility of new functionalities for magnon-based devices, such as spin-wave logic and spin-wave caustic, as well as possible realization of isolators and circulators (see, e.g., [21] and references therein). Recently,

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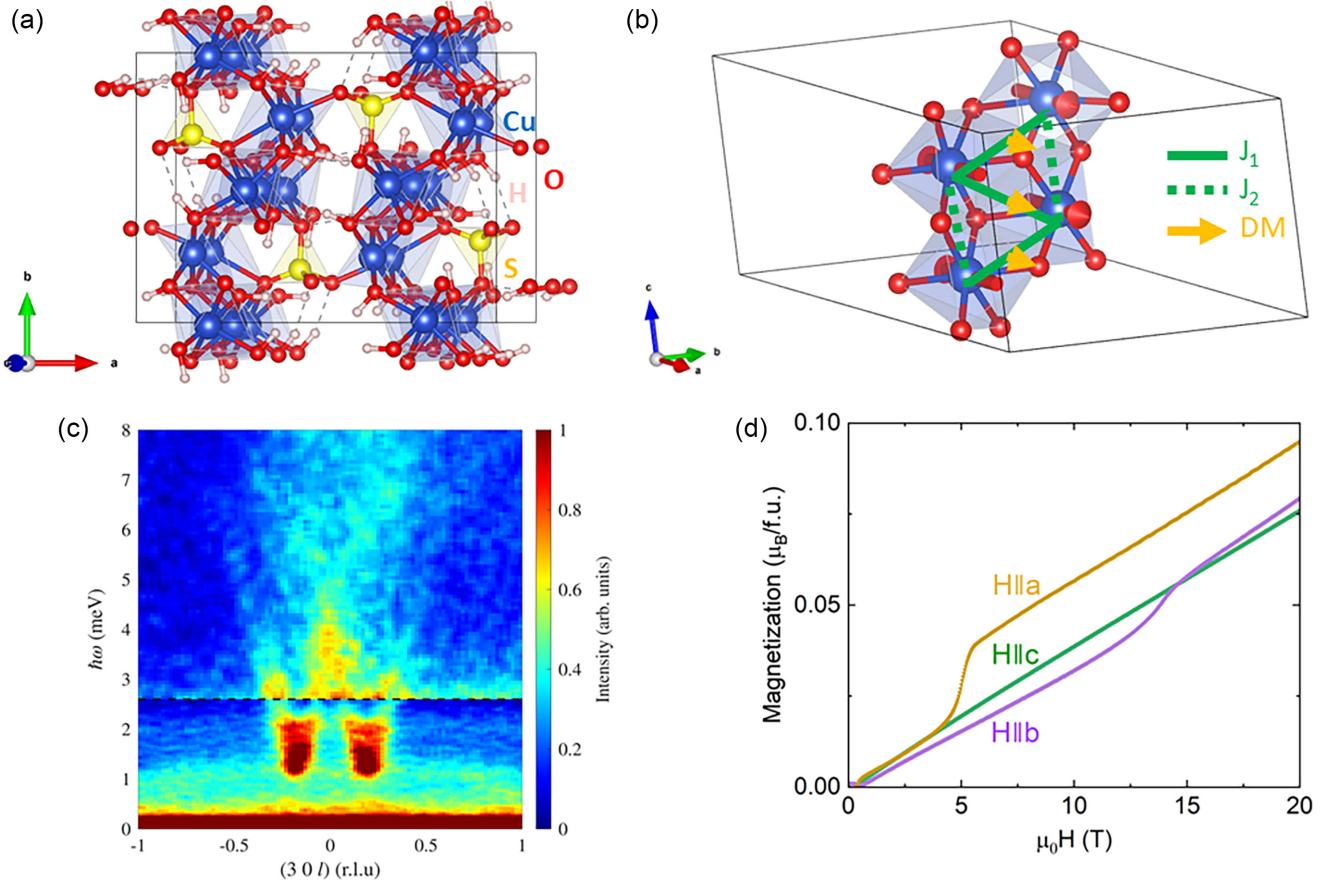


FIG. 1. (a) Crystal structure of brochantite. Edge- and corner-sharing CuO_6 octahedra are shown in light blue and SO_4 tetrahedra are shown in yellow. (b) Single Cu^{2+} zigzag double chain where the main exchange interactions within the chain are shown. (c) Spin-wave dispersion of $\text{Cu}_4\text{SO}_4(\text{OH})_6$ in the AFM state at 1.7 K measured along l direction using Cold Neutron Chopper Spectrometer at the Spallation Neutron Source, Oak Ridge National Laboratory. The spectrum's lower part below the black dashed line was collected with $E_i = 3.32$ meV and the upper part with $E_i = 12$ meV. The data are integrated by ± 0.5 r.l.u. in two orthogonal directions. (d) Magnetization of brochantite measured in pulsed fields applied along principal crystallographic directions.

in addition to ferromagnets (FM) and FM thin films, non-reciprocal magnons were reported for the first time in an antiferromagnet (AFM) $\alpha\text{-Cu}_2\text{V}_2\text{O}_7$ [22]. The advantages of AFM in comparison to FM are higher frequencies and lower damping. As shown below, brochantite shows a number of striking similarities to $\alpha\text{-Cu}_2\text{V}_2\text{O}_7$. Nevertheless, as the crystal structure of brochantite is centrosymmetric it does not allow nonreciprocal magnons in a straightforward way. In this case a full magnetic system (crystal and spin order) should lack any symmetry that maps $\mathbf{k} \rightarrow -\mathbf{k}$.

The most common form of brochantite [Fig. 1(a)], which we refer to in this work, has a monoclinic structure with space group (SG) $P2_1/a$ (No. 14) and lattice parameters $a = 13.140$, $b = 9.863$, $c = 6.024$ Å, $\beta = 103.16^\circ$ [23,24]. There are, however, indications that the true low-temperature symmetry of natural $\text{Cu}_4\text{SO}_4(\text{OH})_6$ could be lower [25,26]. There is also a recent paper on the synthetic single crystals reporting a new brochantite polytype (SG No. 36 with roughly doubled unit cell) with bulk magnetic properties very similar to those reported in the natural mineral [25–27]. Ginga *et al.* reported that monoclinic polymorphs are very similar in terms of their magnetic models, and the occurrence of one or another does not significantly influence their magnetic

properties, consistent with the previous works on the magnetic behavior of brochantite [17]. The main structural components controlling magnetism in brochantite are Cu^{2+} zigzag double chains running along the c axis, turning this material into a low-dimensional quantum magnet [Fig. 1(b)]. These are created by two nearly linear chains of edge-sharing copper octahedra. Along the b direction one double chain is connected to the other by corner sharing, creating corrugated sheets roughly in the bc plane. Along the a direction these sheets are connected through the sulfate groups. Despite its low dimensionality, brochantite orders at low temperatures. Both the temperature dependence of the magnetization and the specific heat show a transition to a magnetically ordered state below about 6 K [16,25,26,28].

Elastic NS clearly points to a commensurate (CM) magnetic order in $\text{Cu}_4\text{SO}_4(\text{OH})_6$ [16,25,26]. The best model based on a limited single-crystal data set suggested zigzag AFM chains coupled antiferromagnetically [25,26]. The Cu moment is significantly reduced, $m_{\text{Cu}} = 0.3 \mu_B$, and is predominantly aligned along the a axis. The most striking observation is that spin dynamics in brochantite is dominated by strong gapped magnonlike excitations along the l direction centered at the incommensurate (ICM) positions $l = 0.19$ r.l.u.

(reciprocal lattice units), suggesting spiral spin-chain dynamics in spite of static CM long-range AFM order [Fig. 1(c)] [25,26]. Despite this complex crystal structure, however, the main features of spin dynamics can be explained using a relatively simple $S = \frac{1}{2}$ XXZ AFM Heisenberg chain model with dominant nearest-neighbor interaction $J_1 = 10.6$ meV, easy-axis anisotropy $\delta = 1.05$, and antisymmetric DMI = 3 meV. DFT+ U calculations taking into account higher-neighbor interactions essentially confirm the inelastic neutron data and report that the J_1 interaction is larger than all the others by a factor from 3 to 100 [17,25,26].

One of the main issues remaining with respect to the magnetic properties of $\text{Cu}_4\text{SO}_4(\text{OH})_6$ is the presence of a metamagnetic transition when magnetic field is applied along the a and b axes with critical fields $\mu_0 H_a = 5$ T and $\mu_0 H_b = 13.9$ T [Fig. 1(d)], respectively [25–27]. These cannot be explained either by the collinear magnetic structure reported by Nikitin *et al.* or by its modified version assuming a small rotation toward the b axis [25–27]. While the transition along the b axis looks as a spin-flop transition since the value of H_b agrees well with a Zeeman energy of 1.5 meV corresponding to the observed gap, this is not the case for $H \parallel a$. For the a axis the critical field is only one third of that along the b , whereas the magnetization roughly doubles across the metamagnetic transition. In addition, below $\mu_0 H_a = 5$ T the magnetization along the a axis and the hard direction c axis are comparable, while above H_a the magnetization along the a axis is enhanced and remains larger than that along the c axis up to 30 T. This contrasts with the b axis, where the magnetization along b is lower than that along c up to H_b and reaches the same level at the transition. A possible explanation may be that the Cu ions create two magnetic subsystems which react to the magnetic field independently. Recent work on synthetic single crystals indicates a double transition at T_N in the heat capacity measurements, which might be considered in favor of the above scenario [27]. Alternate scenario with one magnetic subsystem would require more complex noncollinear magnetic structure.

Clearly, addressing these issues requires examining the details of the magnetic ground state and understanding the mechanism behind the field-induced transitions. In this work we investigate the response of brochantite to high-magnetic fields using an extended range of experimental techniques including magnetization, specific heat (SH) measurements, and nuclear magnetic resonance (NMR). The field was applied both along principal crystallographic directions and in-between them. Based on these results a detailed H - T phase diagram is constructed. We performed polarized NS measurements giving us access to a weak magnetic signal on the top of nuclear reflections. Their outcome unambiguously demonstrates that the ground state in brochantite is a noncollinear magnetic order constrained in the ab plane. The proposed magnetic structure is consistent with the field-induced transition observed in the ab plane. The critical field and character of this transition strongly depend on the field direction. While the $H \parallel b$ limit is consistent with a spin-flop-like response, the $H \parallel a$ one is more closely related to the correlated regime above the ordering temperature. Our results reveal that the ground-state and field-induced phases in $\text{Cu}_4\text{SO}_4(\text{OH})_6$ cannot be explained by a simple XXZ model with a single dominant

exchange interaction, and one to two orders of magnitude weaker interactions have to be also taken into account.

II. EXPERIMENT

High-quality natural single crystals of $\text{Cu}_4\text{SO}_4(\text{OH})_6$ were obtained commercially. They originate from the Milpillas Mine, Cuitaca, Sonora, Mexico. The largest crystal (350 mg), used in this work for neutron scattering experiments, is the same as the one utilized in our previous work, Refs. [25,26]. Sample characterization is provided in the Supplemental Material (SM) and in the above work [29].

The SH measurements were carried out at the High Field Laboratory for Superconducting Materials (HFLSM) at the Institute for Materials Research (Tohoku University, Japan). The SH was measured by the long-relaxation (dual-slope) method designed for a two-axis rotator [30]. A bare-chip resistive thermometer (Cernox 1030BR) was used as both thermometer and heater [31]. The thermometer was calibrated in magnetic fields up to 24 T at 0.5, 1.4, and 4.2 K. The sample was directly attached to the bare chip using Apiezon grease for good thermal contact. The holder was rotated by a two-axis rotator inserted in the 25 T cryogen-free superconducting magnet (25T-CSM). The angle of the chip was measured by two Hall sensors placed orthogonally on the rotator. In this way, the complete SH vs temperature dependence was mapped out for the selected fields applied in the a^*b and bc planes, where a^* is a reciprocal lattice axis perpendicular to both b and c axes. Additional SH measurements down to 0.3 K and up to 9 T were conducted using a Physical Property Measurement System (PPMS) at Japan Atomic Energy Agency (JAEA) in Tokai, Japan.

Magnetization measurements were performed using the PPMS at the CoreLab Quantum Materials, Helmholtz-Zentrum Berlin für Materialien und Energie (HZB). Measurements of the angle dependence of the magnetization in the ab plane were achieved by manual regluing the crystal with a precision of 1° – 3° .

The proton (^1H) NMR (nuclear spin $I = \frac{1}{2}$, gyromagnetic ratio $\gamma = 42.577$ MHz/T) measurements were carried out using the 15T-SM superconducting magnet and ^4He refrigeration system at the HFLSM. The NMR coil was made of copper, and ^{27}Al NMR from an aluminum foil inserted into the coil was used to calibrate the exact magnetic field center at the sample position. The experiment was performed by fixing the frequency of the alternating external magnetic field to $f = 149.65$ and 315.1 MHz and scanning the external dc magnetic field applied along the a^* and b axes. The measurements were run for the two magnetic field regions, below and above the critical field $\mu_0 H_a = 5$ T, and the temperature dependence of the NMR signal was followed from 150 down to 1.7 K. The NMR spectra were measured using the general spin-echo method. The $\pi/2$ pulse length was 3 μs and each spectrum tracked the peak position.

The polarized neutron scattering experiment was performed using the thermal triple-axis spectrometer TAS-1 installed in the reactor hall of the research reactor JRR-3 of JAEA. The spectrometer was operated in elastic mode with $E_i = E_f = 14.7$ meV using the double-focusing Heusler (111) monochromator and analyzer. Higher-order contamination

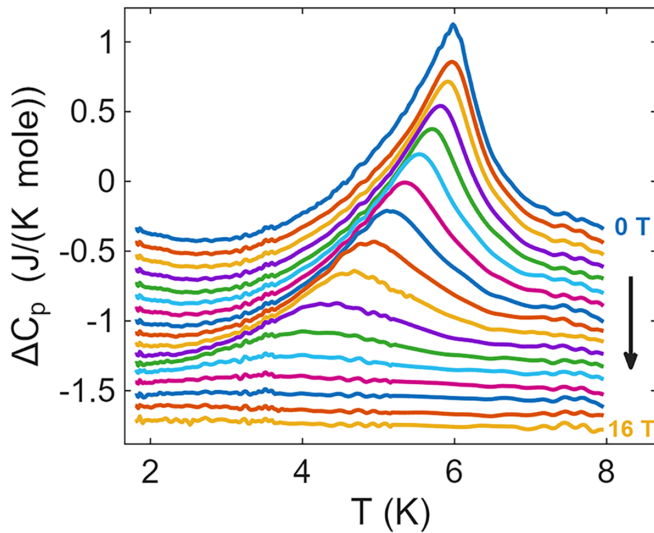


FIG. 2. Temperature dependence of the specific heat at different fields $H||b$ from 0 (the uppermost curve) up to 16 T (the lowermost one) with a step of 1 T. For clarity, the C_p curves are presented as $\Delta C_p = C_p(T, H) - C_p(T, 24.1 \text{ T})$ and vertically offset by equal increments.

was suppressed by a PG filter placed in front of the sample. Longitudinal polarization analysis was achieved using a Mezei-type flipper placed in front of the sample while the Helmholtz coil provided the field parallel to the scattering vector $\mathbf{Q}$ (P_x channel) at the sample position. The 350-mg sample of brochantite used in our previous work was aligned within the $(h k 0)$ -scattering plane and placed into the cryogen-free variable temperature top-load cryostat (Cryogenic) [32].

Additional elastic and inelastic neutron measurements were performed on the time-of-flight (TOF) Cold Neutron Chopper Spectrometer (CNCS) [33,34] at the Spallation Neutron Source, Oak Ridge National Laboratory. The same crystal as above was mounted on an aluminum sample holder and aligned in the $(h k 0)$ -scattering plane. All measurements were performed at temperatures of 1.7 and 15 K using a standard orange cryostat.

For data reduction, analysis and refinement we used the MANTID and FULLPROF software packages [35,36]. The crystal and magnetic structures presented in this paper were drawn using the VESTA visualization program [37].

III. RESULTS

A. Bulk properties

We start by presenting the SH data of $\text{Cu}_4\text{SO}_4(\text{OH})_6$ measured in high magnetic fields up to 24.1 T. At zero field (see Fig. 2), a sharp λ -shaped peak was observed at $T_N = 6 \text{ K}$ indicating a transition to the magnetically ordered state, in agreement with our current and previous measurements [16,25,26,28]. A double transition into the magnetically ordered state has been reported in recent work on synthetic single crystals [27]. However, our zero-field data did not clearly resolve it [25,26].

We continue with the field dependence of the SH for the fields applied along the principal crystallographic directions. The single curves are presented in Fig. 2 for $H||b$ and the

three-dimensional (3D) maps for all field directions are displayed in Fig. 3. In the case of $H||a$ or b axis, the anomaly shifts down to lower temperature, which is typical for AFM. Specifically for the magnetic field applied along the a direction [Fig. 3(a)], where a metamagnetic transition has been observed at 5 T [Fig. 1(d)], the peak becomes broader and is rapidly suppressed for the fields above 4 T. In the extended temperature range down to 0.3 K, no anomalies were observed in the field range between 5 and up to 9 T (not shown). The higher-field data for $H||a$ have no pronounced anomalies. Keeping in mind that $\text{Cu}_4\text{SO}_4(\text{OH})_6$ has monoclinic symmetry, we have carried out the same type of SH as well as magnetization measurements for $H||a^*$. Since no substantial differences had been observed, the $H||a^*$ data yield results equivalent to that for $H||a$, and in the following they are used interchangeably.

For the magnetic field applied along the b direction [Figs. 2 and 3(b)], the peak becomes broader and less intense. However, the anomaly can be followed up to about 13 T, where it disappears. No further anomalies can be detected for $H||b$ up to 24.1 T. The situation is different for the field applied out of plane, where no changes in the SH anomaly were observed up to the highest applied field [Fig. 3(c)].

In the following step, we present the results of the SH measurements for selected fields applied along different crystallographic directions. In all the cases presented in Figs. 3(d)–3(f), an overall data symmetry with respect to the field direction around 0° (as defined below) is observed. At 3.5 and 9 T, i.e., at $H < H_a$ and $H_a < H < H_b$ [Figs. 3(d) and 3(e)], we looked into the SH response to the magnetic field applied in the a^*b plane. Here, the angle setting around 0° corresponds to the field applied along the a^* axis, and $\pm 90^\circ$, where a strong peak in SH is observed, corresponds to the field along the b axis. The peak intensity decreases as the field deviates from this axis, and the peak moves to lower temperatures. At $\mu_0 H = 3.5 \text{ T}$, the peak can be observed in the entire angular range between 5 and 6 K, as shown in Fig. 3(d). In the extreme case, when the field is applied along the a^* axis (0° settings), the intensity is minimal and the anomaly is shifted down to 5.5 K, in agreement with Fig. 3(a). At $\mu_0 H = 9 \text{ T}$, the SH intensity is centered around $\pm 90^\circ$ and a small angular range around it, where it can be followed down to the lowest temperatures [Fig. 3(e)]. At $\pm 90^\circ$, i.e., with the field applied along the b axis, the peak is weak and appears shifted from T_N down to 5 K [see also Fig. 3(b)]. With the field applied off the b axis, the peak intensity is reduced and its position shifts to lower temperatures. For a field offset of $\pm 30^\circ$ the peak is observed at the lowest temperature, while for larger angular offsets no transition can be detected. The absence of the SH anomaly around $0^\circ \pm 60^\circ$ in the whole temperature range below 8 K is due to the fact that the low-field phase at $H||a^*$ has already been suppressed. Indeed, at 30° off the b axis, the field component along a^* already amounts to 4.5 T, i.e., approaching H_a .

Finally, the magnetic phase boundaries in the bc plane were investigated at 20 T, above H_b , as visualized in Fig. 3(f). Here, the data qualitatively resemble those at 9 T for H in the a^*b plane: With increasing the offset angle from the c axis, the peak shifts to lower temperatures, and its intensity is reduced. Initially, a strong SH peak is observed at the angle settings

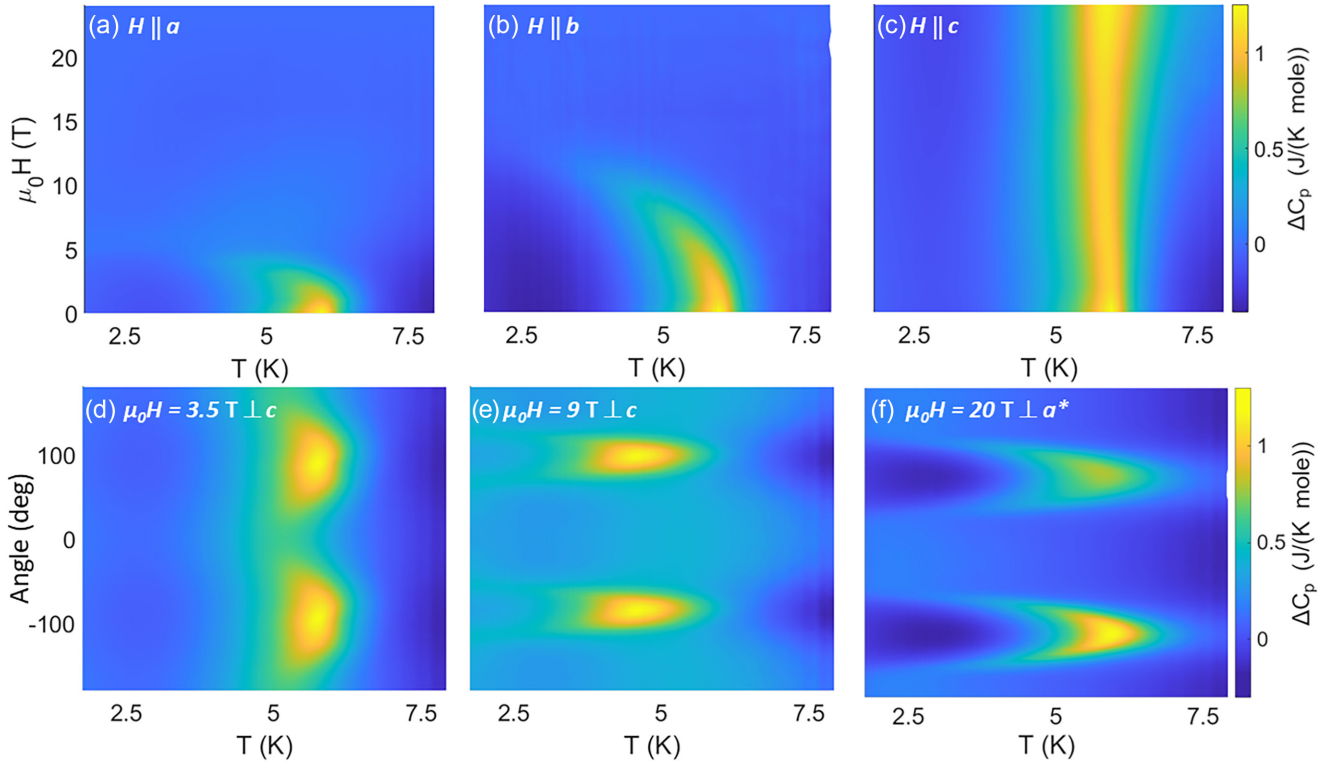


FIG. 3. Specific heat data presented in form of temperature-field (a)–(c) and temperature-angle (d)–(f) color maps: (a)–(c) C_p for $H \parallel a$, b , and c , respectively; (d), (e) C_p for $\mu_0 H = 3.5$ and 9 T $\perp c$, respectively; (f) C_p for $\mu_0 H = 20$ T $\perp a^*$; there is a slight angular misalignment in plane for $H \perp a^*$ resulting in unequal SH intensities at positive and negative angles. For clarity, the C_p curves are presented as $\Delta C_p = C_p(T, H) - C_p(T, H \parallel a = 24.1$ T).

–105° and 75°, which corresponds to the field applied along the c axis. With the field deviating from the c axis, the SH peak shifts to lower temperatures and loses its intensity. The peak is observed at the lowest temperature for the field offset of $\pm 45^\circ$, while no transition can be detected for larger angular offsets. The absence of the SH anomaly at these higher angles below 8 K is a result of suppression of the low-field phase at $H \parallel b$ above 14 T, as can be seen from Fig. 3(b). At 45° off the c axis, the field component along b amounts to ≈ 14 T, close to H_b .

Summing up the above results, a continuous variation of the SH anomaly as a function of temperature and field for different angles is detected, suggesting that we are dealing with a single magnetic sublattice arranged in a noncollinear fashion. To evaluate this scenario, we performed angle-dependent magnetization measurements presented in Fig. 4. The field was applied along the a^* and b directions and at several intermediate angles. Previous results are readily reproduced for $H \parallel a$ and $H \parallel b$ [see Fig. 1(c)], showing minimal and maximal critical fields, respectively. A single transition with critical fields lying in-between H_a and H_b was found for intermediate field directions in the a^*b plane. As the inset in Fig. 4 shows, the critical field of the transition varies smoothly with the angle of the applied field, confirming a single magnetic system with a noncollinear moment arrangement.

Based on the SH and magnetization data, a magnetic H - T phase diagram has been constructed as displayed in Fig. 5. In zero field the AFM phase is observed below 6 K. When the field is applied within the ab plane there is a metamagnetic

transition whose critical field strongly depends on the field direction: it is minimal, $\mu_0 H_a = 5$ T, for $H \parallel a$ and reaches maximum, $\mu_0 H_b = 13.9$ T, for $H \parallel b$. For the field applied along intermediate directions in the ab plane the transition field varies smoothly and lies between H_a and H_b suggesting

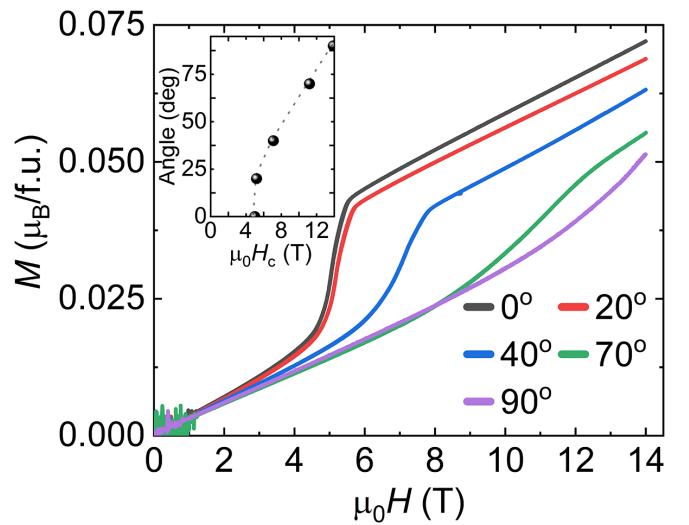


FIG. 4. Field dependence of the magnetization measured in dc magnetic fields along different directions in the a^*b plane. Zero degrees corresponds to the field along the a^* axis. The inset shows the angle dependence of the critical field. The dashed line is a guide to the eye.

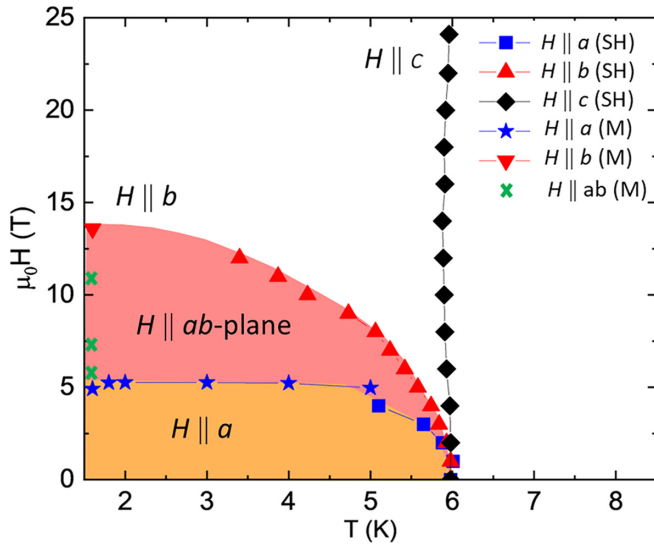


FIG. 5. The H - T phase diagram of brochantite based on the specific heat and magnetization data for magnetic fields applied along principal crystallographic directions and in the ab plane. The symbols are derived from the experimental data and the lines are guides to the eye.

that the Cu moments are confined within the plane. For $H \parallel c$ no field-induced anomalies are detected up to 24.1 T.

B. Polarized neutron scattering

Having established that the high-field magnetic properties of brochantite comply with a noncollinear magnetic order, we have revisited its magnetic structure using polarized neutron diffraction. The problem studying this material using unpolarized neutron diffraction is caused by the combination of the reduced Cu moment and the propagation vector $\mathbf{k} = (0, 0, 0)$, which results in weak magnetic contributions appearing on top of strong nuclear peaks. Figure 6 displays the unpolarized TOF data measured using the CNCS spectrometer at SNS in

the form of $(h k 0)$ scattering maps above and below T_N . As one can see, the neutron intensities are dominated by nuclear scattering. No extra superlattice reflections were detected. On the contrary, polarized neutron scattering allows unambiguous separation of nuclear and magnetic scattering contributions. In longitudinal polarization analysis using the P_x configuration, the non-spin-flip (NSF) channel measures purely nuclear scattering, while the spin-flip (SF) channel selectively probes the magnetic one.

The magnetic intensity in the P_x SF channel is readily observed at 1.6 K, in the magnetically ordered phase, in the $(1\ 2\ 0)$ reflection [see the inset of Fig. 7(a)] similar to the previous unpolarized neutron diffraction results [25,26]. To make sure that the observed intensities are related to magnetic order, we consistently performed temperature scans up to 9 K, across the T_N , where the magnetic intensities should disappear [Figs. 7(a) and 7(b)]. For comparison, we present the intensity of the $(1\ 2\ 0)$ peak in the NSF channel, which probes nuclear scattering and, as expected, does not show any temperature evolution below 10 K. Using the magnetic scattering in the P_x SF channel, we could detect magnetic signals that would otherwise be obscured by the overlap with strong nuclear reflections, in particular $(2\ 0\ 0)$ [see Fig. 7(b)]. The latter is especially important, as it directly points to the presence of the magnetic moment component along the b axis. Strictly speaking, this signal points to a magnetic moment perpendicular to $\mathbf{a}^*$, but the P_z channel data (neutron spin perpendicular to $\mathbf{Q}$ and normal to the horizontal plane), as shown in the SM, do indeed show absence of the moment component along the c direction [29].

In this way, we mapped an extended range of reciprocal space, shown in Fig. 7(c), where intensity differences between the 1.6- and 9-K data are displayed for the P_x SF channel. In total, we collected 23 reflections to model the magnetic structure. This is still a small number given the low symmetry and four Cu sites in the general position, but it allows us to significantly improve the magnetic structure model, as shown below.

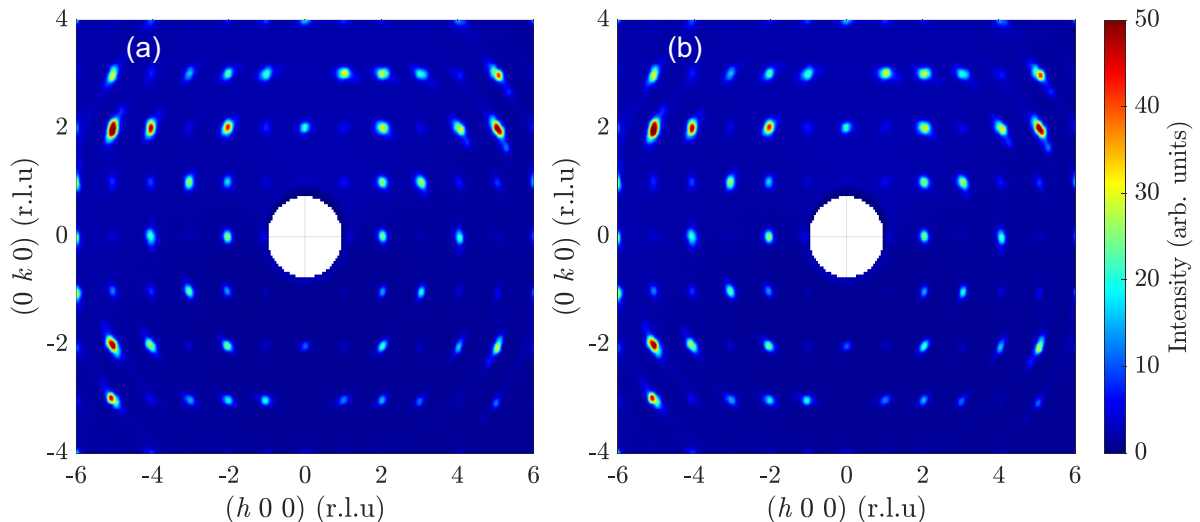


FIG. 6. The elastic neutron scattering map measured in the $(h k 0)$ plane taken with an incident energy $E_i = 12.0$ meV ($\lambda = 2.61$ Å) at (a) $T = 1.7$ K and (b) $T = 15$ K, integrated over an energy-transfer range of $E_f = -0.1$ to 0.1 meV.

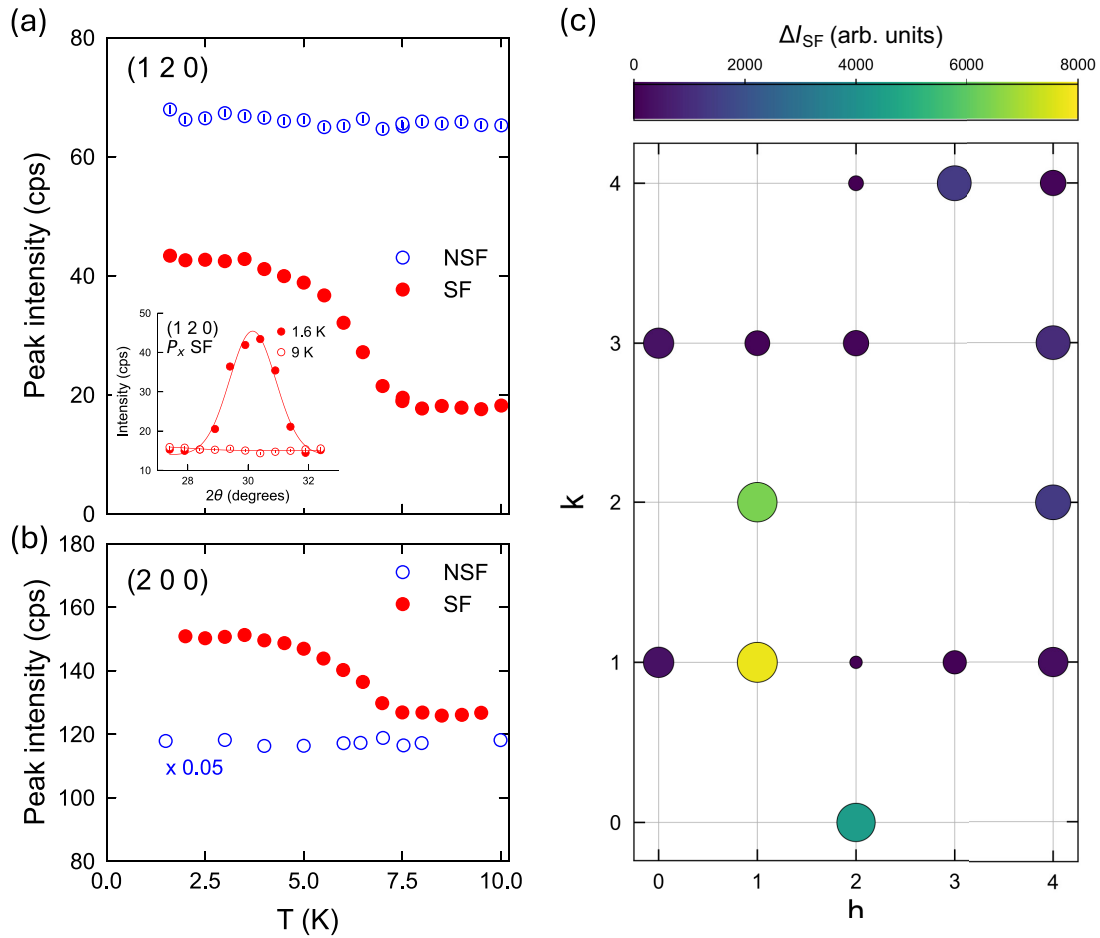


FIG. 7. (a), (b) Temperature dependence of the P_x SF and NSF intensities of selected reflections in brochantite as measured with the TAS-1 spectrometer at JRR-3. The inset of (a) is the SF peak profiles of the (1 2 0) reflection. (c) The $(h k 0)$ color map of all the collected reflections in $\text{Cu}_4\text{SO}_4(\text{OH})_6$. The P_x SF intensities are presented as the difference between 1.6 and 9 K, ΔI_{SF} , i.e., the intensities in the magnetically ordered state minus those in the paramagnetic state, and the marker sizes are proportional to $\log \Delta I_{SF}$.

In order to further quantify the results, we ran a number of measurements in the paramagnetic state at 50 K. The flipping ratio obtained, defined as the ratio between the intensities in the NSF and SF channels, was found to be around 20. The intensities were corrected for instrumental imperfections using the procedure described in Refs. [38–40].

C. Magnetic structure analyses

The details of the crystal structure and the magnetic representation analysis using the parent $P2_1/a$ space group were obtained previously using single-crystal neutron diffraction [25,26]. Therefore, only the scaling factor was adjusted here based on the data collected in the paramagnetic state. However, even given the symmetry constraints, the number of refinable parameters for four magnetic ions in the general position is too large for the set of magnetic reflections obtained. We, therefore, assumed that the Cu moments on different sites are equal, which is reasonable if the deviation between the moment sizes is not large. This reduces the number of parameters to four, which are the angular positions within the ab plane for each Cu spin. Refinement was performed for

different values of the magnetic moment ranging from 0.1 up to the Cu^{2+} theoretical maximum of $1 \mu_B$, as can be expected in the materials containing Cu^{2+} ions (see, e.g., Refs. [41–45]). More details on the refinement and its results are provided in the SM [29].

The best results were obtained for the irrep Γ_4 , corresponding to the magnetic space group $P2'_1/a$. This is in agreement with our previous work, where only the a component of the magnetic moment was considered [25,26]. This time, however, the b component could be clearly identified as visualized in Fig. 7(b) and included in the calculations.

Because of the cross correlation between the size and orientation of the spin, a range of magnetic moments from about 0.45 to $0.9 \mu_B$ was found to have almost the same reliability factors of the obtained magnetic structures. The resultant structures showing the most symmetric moment arrangement are displayed in Fig. 8. In the first case [Fig. 8(a)], the moments within each zigzag chain are aligned in two linear FM chains with an angle of about 90° between them. The refined Cu moment is reduced to $0.47(1) \mu_B$. In the second, the linear chains consist of noncollinear $0.70(1) \mu_B$ moments rotated by about 90° relative to each other. The adjacent moments

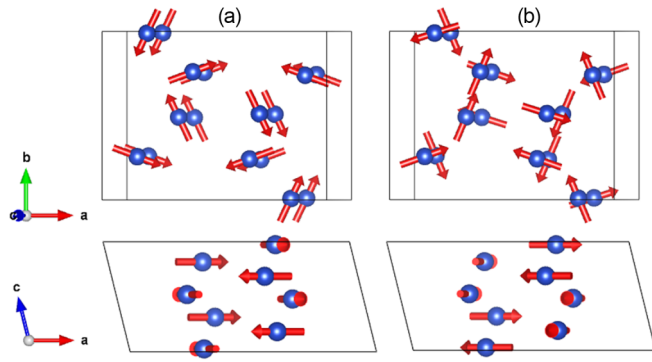


FIG. 8. (a), (b) The models of magnetic structures of brochantite obtained from single-crystal refinement of polarized neutron data. The top row represents the corresponding structures as viewed from the c^* axis while the bottom displays the magnetic unit cells as seen from the b axis. In the latter case only two out of four zigzag chains are shown. The structures' description and the way they were obtained are given in the main text and the SM. The reliability factors R_{wF^2} amount to 19 and 14.4 for the models in (a) and (b), respectively.

between the linear chains are coupled either AFM or FM [Fig. 8(b)]. We note that both FM and AFM J_2 interactions were reported from *ab initio* calculations [17].

Although neither of these structures is a unique solution, they can still be used to identify a few important characteristics of $\text{Cu}_4\text{SO}_4(\text{OH})_6$. First, all the structures have noncollinear moment arrangement within the chains. Second, the moments are arranged such that the angle between them is close to 90° . Finally, while the magnetic structures describe the polarized neutron diffraction data, it is not straightforward to combine them with the INS data [25,26]. Indeed, the experimental inelastic spectrum suggests a dominant AFM exchange interaction J_1 between two otherwise FM chains, combined with an antisymmetric DM interaction pointing along the easy axis. Obtaining the zigzag chains shown in Fig. 8 from the above parameters does not work out in a simple way, suggesting that further investigations are required.

To address this issue, we tried to solve the magnetic structure using space group $P-1$, with 16 independent magnetic ions. Based on the INS data, the only constraint applied was that the Cu moments in the zigzag chains should remain collinear and AFM coupled. This reduces the problem to two independent parameters per chain (eight parameters in total), namely, the magnetic moment and its angular position within the ab plane. Refinement using this model resulted in reliability factors that were significantly worse than that in the models presented in Fig. 8.

D. Proton nuclear magnetic resonance

To get further insights into magnetic structure of brochantite, we performed (^1H) NMR measurements on a single crystal. We focused the measurements on $H \parallel a^*$ and $H \parallel b$ since these directions exhibit the most pronounced anisotropic features in the low-temperature magnetization and are therefore the most relevant for establishing the phase diagram. By contrast, for $H \parallel c$, no clear anomaly was resolved in the

measured field range of the low-temperature M - H data. The results are summarized in Fig. 9. Figures 9(a) and 9(b) show the field-swept (^1H) NMR spectra for $H \parallel a^*$ measured at fixed frequencies of $f = 149.65$ and 315.1 MHz, respectively. Figure 9(c) shows the field-swept (^1H) NMR spectra for $H \parallel b$ measured at a fixed frequency of $f = 149.65$ MHz.

First, we discuss the spectral line shape in the paramagnetic state. For protons with nuclear spin $I = \frac{1}{2}$, there is no quadrupolar interaction, and thus no EFG-related (electric field gradient) splitting or asymmetry. Therefore, the (^1H) NMR spectrum directly reflects the distribution of the effective local magnetic field at the proton sites: in the paramagnetic state it provides a site-resolved map of crystallographically distinct proton environments, whereas in the magnetically ordered state it probes the distribution of internal fields. As shown in Figs. 9(a)–9(c), at a temperature well above T_N ($T = 100$ K), the (^1H) NMR spectrum exhibits a line shape that is well described by a superposition of two Gaussian components. The crystal structure of brochantite $\text{Cu}_4\text{SO}_4(\text{OH})_6$ contains six crystallographically distinct H sites. In principle, the (^1H) NMR spectrum should therefore consist of six overlapping site-resolved contributions; nevertheless, the experimental spectrum is captured by only two Gaussian components. This indicates that the proton local environments are effectively grouped into two classes. To clarify the microscopic origin of this classification, we note that each proton exists as part of an O–H group, and its hyperfine coupling is expected to be dominated by the electronic environment of the nearest oxygen atom. It is therefore natural to characterize the proton sites in terms of how the corresponding oxygen in the O–H group is coordinated to nearby Cu ions. The corresponding O–H local geometries, illustrated for the same crystal orientation, are shown schematically in Fig. 9(d). As illustrated in this way, the distinction becomes clear: the O–H1–O–H4 groups have three effectively coordinating Cu ions, whereas the O–H5 and O–H6 groups have only two. Moreover, the Cu–O bond lengths associated with O–H5 and O–H6 are shorter, suggesting that the hyperfine coupling at H5 and H6 should be larger than that at H1–H4.

For $H \parallel a^*$, as shown in Figs. 9(a) and 9(b), the double-Gaussian spectrum appears to undergo an additional splitting into three components below ~ 20 K. One possible origin is a weak differentiation within the threefold-coordinated O–H groups: because the O–H lengths for O–H1 (0.844 Å) and O–H3 (0.914 Å) are shorter than those for O–H2 (1.074 Å) and O–H4 (0.981 Å), their hyperfine couplings are expected to be slightly larger, which could account for the observed splitting. However, it is important to note that for $T \gtrsim 20$ K the spectral line shape, including the peak positions, remains essentially unchanged. Below ~ 20 K, the spectrum begins to evolve abruptly, as if an additional hyperfine (internal) field suddenly develops. This behavior can be attributed to the development of short-range order (SRO) above $T_N(H)$, likely reflecting the formation of low-dimensional AFM correlations, as reported in Refs. [16,25,26]. Notably, for $H \parallel b$ [Fig. 9(c)], no comparable SRO-related spectral evolution is observed below $T \sim 20$ K: the double-Gaussian line shape remains essentially unchanged down to just above $T_N(H)$. Below $T_N(H)$, the spectrum broadens due to the emergence of internal fields.

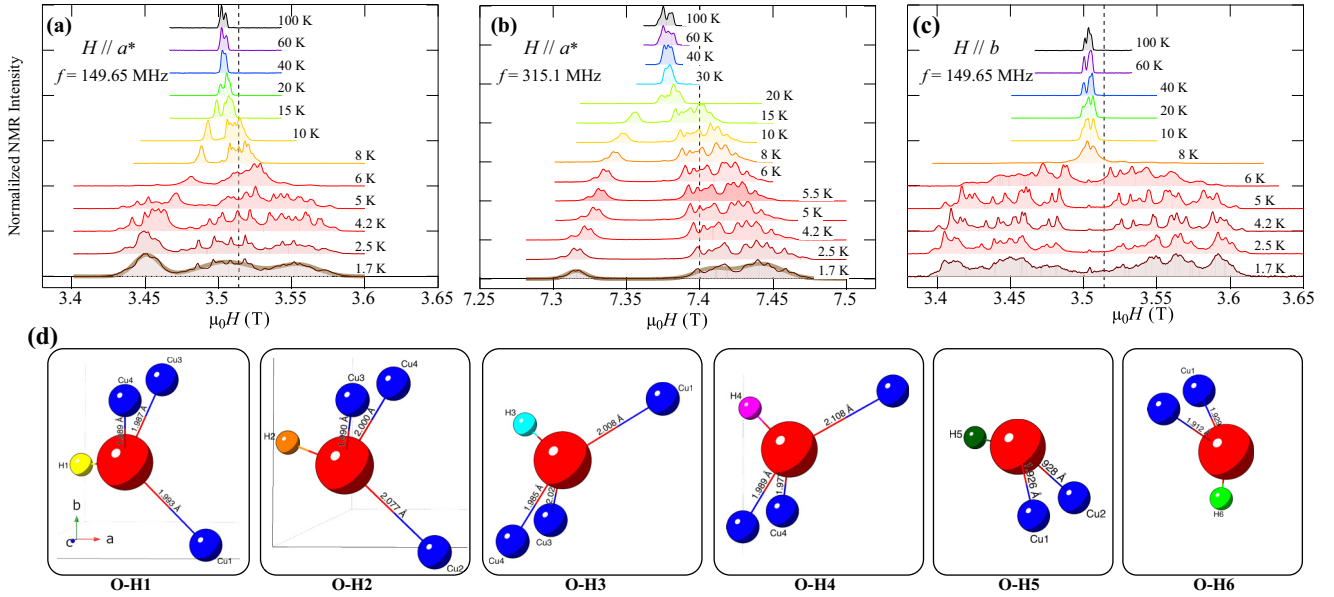


FIG. 9. Field-swept (^1H) NMR spectra of brochantite $\text{Cu}_4\text{SO}_4(\text{OH})_6$ measured at fixed frequencies. For clarity, representative spectra at selected temperatures are shown and are vertically offset by equal increments. The NMR intensities are normalized. (a) $f = 149.65$ MHz for $H \parallel a^*$. The vertical dotted line indicates the Larmor field $H_0 = f/\gamma$. (b) $f = 315.1$ MHz for $H \parallel a^*$. The thick brown curves for the $T = 1.7$ K data in (a) and (b) are guides to the eye. (c) $f = 149.65$ MHz for $H \parallel b$. (d) Schematic illustrations of the local environments of the O-H groups associated with the crystallographically distinct H sites, shown for the same crystal orientation.

As shown in Fig. 9(a), further line broadening and additional splittings are observed below $T_N(H) \simeq 6$ K, where long-range AFM order emerges. Since these spectra were measured at fields below the critical field, $\mu_0 H_a \sim 5$ T, for $T < T_N$, they reflect the low-field phase. If the previously proposed collinear AFM order [25,26] were realized, each of the three classes of (^1H) sites would experience a pair of internal fields $\pm H_i^{\text{int}}$ ($i = 1, 2, 3$). Upon projection onto the external-field direction, this would produce a simple twofold splitting for each class, resulting in a total of six resonance lines. In contrast, the spectrum at $T = 1.7$ K exhibits a substantially more complex pattern, with multiple splittings that appear to overlap and merge. Nevertheless, the spectral intensity remains concentrated into several partially resolved components rather than forming a single smooth continuum typically expected for an incommensurate order with a broad distribution of internal fields; in particular, for $H \parallel b$ the line shape shows more discretized features that are qualitatively compatible with a commensurate-like splitting in agreement with neutron diffraction results of this and previous works [16,25,26]. At the same time, the $H \parallel b$ data are still too complex to be accounted for by the simple collinear twofold-splitting scheme described above. These observations therefore indicate that a collinear AFM structure is not consistent with the NMR spectra.

Finally, we emphasize a key insight obtained from the present (^1H) NMR measurements. Below $T_N(H)$, the spectra exhibit highly complex line shapes. Further measurements and a detailed line-shape analysis will be necessary to determine whether these spectra are consistent with the non-collinear magnetic structure proposed in Fig. 8. Importantly, the spectral evolution that sets in below $T \sim 20$ K, which we attribute to the development of quasistatic AFM short-range

correlations, is clearly observed even in magnetic fields exceeding the metamagnetic critical field $\mu_0 H_a = 5$ T, as shown in Fig. 9(b). Moreover, at $T = 1.7$ K the spectra on both sides of H_a remain multicomponent, and the high-field spectrum does not recover the simple double-Gaussian line shape observed above $T \sim 20$ K. These observations indicate that the correlations responsible for the multicomponent local-field distribution persist into the high-field regime where long-range magnetic order is suppressed. A detailed discussion is given in the next section.

IV. DISCUSSION

Below 6 K in zero field brochantite exhibits a long-range AFM order (see the magnetic H - T phase diagram presented in Fig. 5). Polarized neutron measurements show that the magnetic structure has spin components along both the a and b axes. The exact type of magnetic order is impossible to deduce based purely on the measured neutron scattering data, but all the refinements point to a noncollinear magnetic structure. One of the best results is given in Fig. 8. Here, the moments within the double chains are noncollinear, either collinear FM chains rotated to each other by roughly 90° or noncollinear chains with the moments coupled both FM and AFM.

Obviously, the magnetic order obtained is not fully compatible with the oversimplified XXZ AFM Heisenberg chain model with dominant nearest-neighbor interaction J_1 [25,26]. Indeed, the presence of the noncollinear spin arrangement on the level of the zigzag chains implies that a single J_1 within the chain is not enough to describe the magnetic order and has to be complemented by next-nearest-neighbor interactions within and between the planes. This is not surprising, as $\text{Cu}_4\text{SO}_4(\text{OH})_6$ shows a 3D magnetic order in the ground state.

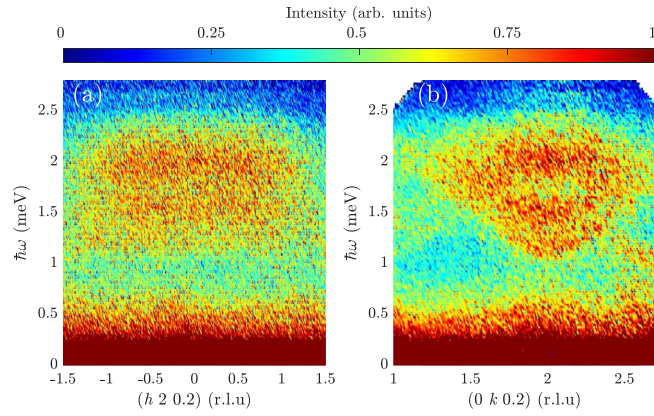


FIG. 10. Magnetic excitations in brochantite measured with incident energy $E_i = 3.32$ meV at 1.7 K along the h (a) and k directions (b), respectively, using CNCS spectrometer.

In agreement with this, about an order of magnitude smaller (compared to J_1) but still finite dispersion along the b and a directions was detected in our previous INS measurements [25,26]. Experimental dispersion bandwidths are shown in Figs. 1(c) and 10. We note that additional measurements of the temperature dependence of the gap mode show that the gap decreases on warming and closes on approaching T_N . This behavior is more naturally consistent with an anisotropy-induced magnon gap associated with the ordered state than with a simple singlet-triplet excitation of a spin-dimer ground state. Figures 1(c) and 10 provide a useful hierarchy of energy scales: a dominant nearest-neighbor exchange along the chains in the c direction, $J_1 \approx 10$ meV, a much smaller interchain coupling roughly along b , $J_b \approx 1.5$ meV, and a very weak coupling roughly along a , $J_a < 0.5$ meV, where the Cu sheets are connected through the sulfate groups [25,26]. In this respect, it is worth recalling that above $T_N(H)$, our NMR data for $H \parallel a^*$, together with the specific heat and magnetization data reported in Refs. [16,25–27], indicate the presence of SRO. Within the H - T phase diagram of Fig. 5, this regime is best regarded as a crossover region located in the vicinity of the long-range-ordered phases, rather than as an independent thermodynamic phase. The SRO inferred from the NMR and bulk data is characterized by quasistatic antiferromagnetic correlations. Since the weakest exchange is along the a direction, i.e., between the bc sheets, these correlations can be naturally interpreted as quasi-two-dimensional AFM correlations developing within the bc layers.

Turning to the high-field properties (Fig. 5), a metamagnetic transition is observed when the external magnetic field is applied within the ab plane. As can be seen from the data in Figs. 3 and 4, changing the field direction causes a smooth variation of the critical fields and transition temperatures. The critical field and magnetization change across this transition are strongly dependent on the field direction. The lowest critical field $\mu_0 H_a = 5$ T and at the same time the largest change in magnetization (its approximate doubling) are observed for the field applied along the a axis, while for $H \parallel b$ the critical field is the largest, $\mu_0 H_b = 13.9$ T, accompanied by the smallest magnetization increase. The field range between the boundaries defined by $H \parallel a$ and $H \parallel b$ lines in Fig. 5 represents the cases in

which the field is applied in the ab plane with the critical fields $H_a < H < H_b$ and intermediate magnetization jump. Finally, for $H \parallel c$ the zero-field phase with a finite magnetization, presumably induced by a small moment canting off the ab plane, remains stable up to 24.1 T.

The high-field bulk measurements presented here suggest that strong dependence of the magnetic transition on the field direction in $\text{Cu}_4\text{SO}_4(\text{OH})_6$ is related to a non-collinear magnetic structure confined in the ab plane. The proposed magnetic structure (Fig. 8) and the bulk magnetization [Fig. 1(d)] are mutually consistent if one takes into account the anisotropic exchange inferred from the INS dispersions. A full, quantitative model would require additional data to construct a microscopic Hamiltonian including all intrachain and interchain exchange terms and anisotropic exchange contributions. Although that is beyond the scope of this work, some conclusions can still be drawn and a qualitative mechanism proposed.

Obviously, the mechanism of the transition changes when going from one extreme field direction, $H \parallel b$, to the other, $H \parallel a$, given the underlying noncollinear magnetic structure. The phase transition for the former is consistent with a spin-flop-like transition involving weakly coupled chains. It cannot be an ordinary spin-flop transition, as brochantite is not a uniaxial AFM. Nevertheless, half of the Cu moments have a large spin component aligned along the b axis. This has some similarity to green diopside, $\text{Cu}_6[\text{Si}_6\text{O}_{18}] \cdot 6\text{H}_2\text{O}$, another natural Cu^{2+} -based mineral, with different orientations of the local easy axes [46]. There, no sharp phase transition takes place when going from the low-field to the high-field state but rather a strong crossover. Here, the magnetization also shows a spin-flop-like shape with a smooth transition at H_b . Additionally, its energy scale agrees with the inelastic neutron scattering dispersion along the b axis. The magnetization curve suggests that J_b is only weakly anisotropic.

The transition along the a axis should have a different origin. In principle, half of the Cu moments again have a comparably large spin component along the a axis and different orientations of the local easy axes. However, the magnitude of H_a is almost three times smaller while the jump of magnetization at H_a is much larger. The magnetization in this direction is also larger than that for the hard direction, $H \parallel c$, from H_a up to 30 T which is not typical for spin-flop transitions. In Cu oxides, the experimentally observed g factors can be anisotropic, leading to magnetization differences (see, e.g., Refs. [47–49]). The electron spin resonance (ESR) spectrum (not shown) measured at 10 K and 360 GHz in pulsed magnetic fields applied along the a^* axis exhibits a minimum corresponding to the g value of 2.03. This implies that the g factor in $\text{Cu}_4\text{SO}_4(\text{OH})_6$ is very close to the isotropic value, suggesting that this mechanism can be excluded.

An alternative interpretation is suggested by the (^1H) NMR spectra measured both above $T_N(H)$ and at base temperature. For $T \gtrsim 20$ K, the field-swept double-Gaussian-like spectra for $H \parallel a^*$ show no qualitative change in the overall line shape across $\mu_0 H_a \simeq 5$ T. This indicates that the local-field distribution probed by (^1H) NMR remains essentially the same across H_a in this temperature range. In contrast, upon cooling below $T \sim 20$ K the spectrum evolves abruptly into a multi-component line shape, which we attribute to the development

of quasistatic AFM short-range correlations. At $T = 1.7$ K, the low-field spectrum at $\mu_0 H \simeq 3.5$ T shows clearly resolved splittings below $T_N(H)$, consistent with the emergence of long-range order. Above H_a , the spectrum remains multi-component and is broadly consistent with a three-component profile, although the relative peak positions and intensities differ from those in the low-field phase. This persistence of a multicomponent spectrum across H_a disfavors a simple spin-flop scenario for $H \parallel a$. If a spin flop occurred at H_a , the ordered moments would rotate toward the bc plane, which would substantially reduce their projection onto the a axis and would be expected to produce a much simpler (^1H) NMR line shape than observed.

These NMR results therefore suggest that the metamagnetic transition at H_a does not simply transform the low-temperature state into a collinear high-field phase. Rather, the underlying AFM correlations responsible for the multi-component local-field distribution persist into the high-field regime, even where long-range order is suppressed. The field-direction dependence provides additional constraints. For $H \parallel b$, no comparable SRO-related spectral evolution is observed [Fig. 9(c)]. At present, it is not possible to determine whether this reflects an intrinsic anisotropy in the field-induced development of SRO, or whether the SRO is present but its associated hyperfine field has a strong anisotropy so that the relevant component is not captured in the (^1H) spectra for $H \parallel b$. A more detailed microscopic description, together with additional NMR data and line-shape analysis, will be required to establish the nature of the SRO in the high-temperature and high-field regime.

V. CONCLUSION

In conclusion, we have presented the results of comprehensive studies of spin- $\frac{1}{2}$ quantum magnet brochantite $\text{Cu}_4\text{SO}_4(\text{OH})_6$. The phase diagram has been constructed using bulk measurements, showing the main magnetic phases as a function of temperature and magnetic fields up to 24.1 T. Employing polarized neutron scattering the ground-state noncollinear magnetic structure has been proposed, and its connection to the field-induced magnetic phases has been established. The results indicate that the ground-state and field-induced phase transitions cannot be explained using a simple XXZ model with a single dominant J_1 and, further, although one to two orders of magnitude smaller,

exchange interactions have to be taken into account. It is the complex interplay between them combined with the quasi-two-dimensional geometry of the material that produces a rich landscape of magnetic phases.

Our measurements show that brochantite hosts a non-collinear spin arrangement within the zigzag chains and exhibits the field-induced transition for the magnetic field applied in the ab plane. The character of the transition changes for the field applied along the a and b directions. While the latter might be a spin-flop-like transition, the angle-resolved specific heat, magnetization, and NMR data reveal that the transition along the a axis arises from a different mechanism. The high-field state for $H \parallel a$ closely resembles the short-range-correlated regime above T_N , suggesting that the field stabilizes a configuration inherited from quasi-two-dimensional correlations in the bc planes. These results provide a solid basis for developing a full microscopic Hamiltonian and motivate further high-field spectroscopic studies to explore the excitation spectrum in the field-induced phases.

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DATA AVAILABILITY

The data that support the findings of this article are not publicly available. The data are available from the authors upon reasonable request.

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