

Atacamite $\text{Cu}_2\text{Cl}(\text{OH})_3$: A model compound for the $S = 1/2$ sawtooth chain?

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We present a combined experimental and theoretical study of the mineral atacamite $\text{Cu}_2\text{Cl}(\text{OH})_3$. Based on *ab initio* band structure calculations, we derive a magnetic coupling scheme of essentially a $S = 1/2$ sawtooth chain. Experimentally, we fully characterize the long-range antiferromagnetically ordered state and field-induced behavior, here for $H \parallel b$ axis. Magnetic order is suppressed by magnetic fields of ~ 20 T, while beginning at 31.5 T we observe a wide magnetization plateau at half of the saturation magnetization, $M_{\text{sat}}/2$. Numerical calculations for the magnetization $M(H)$ of the quantum sawtooth chain reveal a plateau at $M_{\text{sat}}/2$, raising the issue of the understanding of its microscopic nature.

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Frustrated low-dimensional quantum spin systems offer a unique opportunity to study the ground state properties and excitations of complex quantum systems both from a theoretical and experimental point of view [1–4]. Conceptually, a multitude of models have been introduced by theory, such as the Kagome lattice, the diamond chain or the frustrated J_1 - J_2 chain [5–7]. These are studied with respect to novel and exotic ground and field induced states like spin liquids, magnetization plateaus or nematic phases. Experimental efforts to identify real world materials to test these theoretical concepts are exemplified by work on natural minerals such as herbertsmithite $\text{ZnCu}_3(\text{OH})_6\text{Cl}_2$, azurite $\text{Cu}_3(\text{CO}_3)_2\text{OH}_2$ or linarite $\text{PbCuSO}_4(\text{OH})_2$ [8–11], to name a few. Through this combination of theoretical and experimental studies, utilizing state-of-the-art computational and experimental techniques, a new level of insight into complex topics of quantum magnetism is achieved.

The sawtooth or Δ -chain represents one such seminal model in the field of frustrated quantum magnetism. It consists of a chain of spin triangles, with the Hamiltonian

$$\mathcal{H} = \sum_i J_1 \mathbf{S}_i \mathbf{S}_{i+2} + J_2 (\mathbf{S}_i \mathbf{S}_{i+1} + \mathbf{S}_{i+1} \mathbf{S}_{i+2}) - h S_i^z, \quad (1)$$

where \mathbf{S}_i is the spin-1/2 operator at site i . J_1 represents the interaction between neighboring spins \mathbf{S}_i and \mathbf{S}_{i+2} along the chain axis, while J_2 measures the interaction between spins \mathbf{S}_{i+1} on the triangular sites with the spins $\mathbf{S}_i, \mathbf{S}_{i+2}$ on the chain. The last term accounts for the Zeeman splitting on each site in a magnetic field h .

This model has been studied extensively by theory for decades [12–32]. Motivated by these works, various attempts have been made to identify real world materials

that could be used to test the sawtooth model. However, for none of the materials proposed so far it was possible to ultimately prove this notion [17, 25, 33, 34].

In this letter, based on an extensive and combined experimental and theoretical study, we argue that the natural mineral atacamite, $\text{Cu}_2\text{Cl}(\text{OH})_3$, represents the first realization of a frustrated $S = 1/2$ quantum sawtooth chain. By means of electronic band structure calculations, we derive the magnetic coupling parameters. To leading order, these are understood as that of a sawtooth chain, with a dominant chain coupling $J_1 \sim 100$ K, a sawtooth coupling $J_2 \sim 30$ K and residual interchain couplings of a few K strength. We characterize the magnetic ground state by thermodynamic probes and neutron diffraction, presenting here the data for the magnetic field $H \parallel b$ axis (*viz.*, the chain axis). Our data reveal a magnetically ordered state at $T_N = 8.9$ K $\ll J_1$, as it is typical for frustrated quantum magnets. The ordered state is suppressed by magnetic fields ~ 20 T, while at elevated fields we observe a wide magnetization plateau at half saturation magnetization $M_{\text{sat}}/2$. Numerical simulations of the magnetization demonstrate the existence of a magnetization plateau for the sawtooth chain at $M_{\text{sat}}/2$.

The natural mineral atacamite $\text{Cu}_2\text{Cl}(\text{OH})_3$, named after its discovery location in the Atacama desert and identified as a biomineral [35, 36], crystallizes in an orthorhombic lattice (space group $Pnma$ [37], lattice constants $a = 6.02797$ Å, $b = 6.86383$ Å, $c = 9.11562$ Å; Fig. 1 (a) [38, 39]). In this structure, there are two inequivalent Cu sites (Cu(1) and Cu(2) shown as dark and light blue spheres). By arguing that the structure of atacamite ought to be understood in terms of a network of pyrochlore tetrahedra formed by Cu^{2+} ions the material was

proposed to represent a frustrated magnet [38, 40, 41]. However, this bonding scheme has not been tested experimentally or theoretically so far.

To accurately describe the bonding scheme in atacamite, we have carried out band structure calculations using the full potential local orbital (FPLO) basis set and GGA functional [39, 42, 43]. From these calculations, we find a coupling scheme with four different magnetic exchange paths J_1 – J_4 (Fig. 1 (b)). In Tab. I we summarize the different coupling strengths, depending on the value of the Coulomb repulsion U . The calculations reveal that two of the four exchange constants, *viz.*, J_1 and J_2 , dominate the magnetic behavior, while J_3 and J_4 represent residual coupling strengths in the Kelvin range. If we highlight the view of the crystal structure onto those structural elements involved in the magnetic exchange, a pattern of sawtooth chains aligned along the b axis

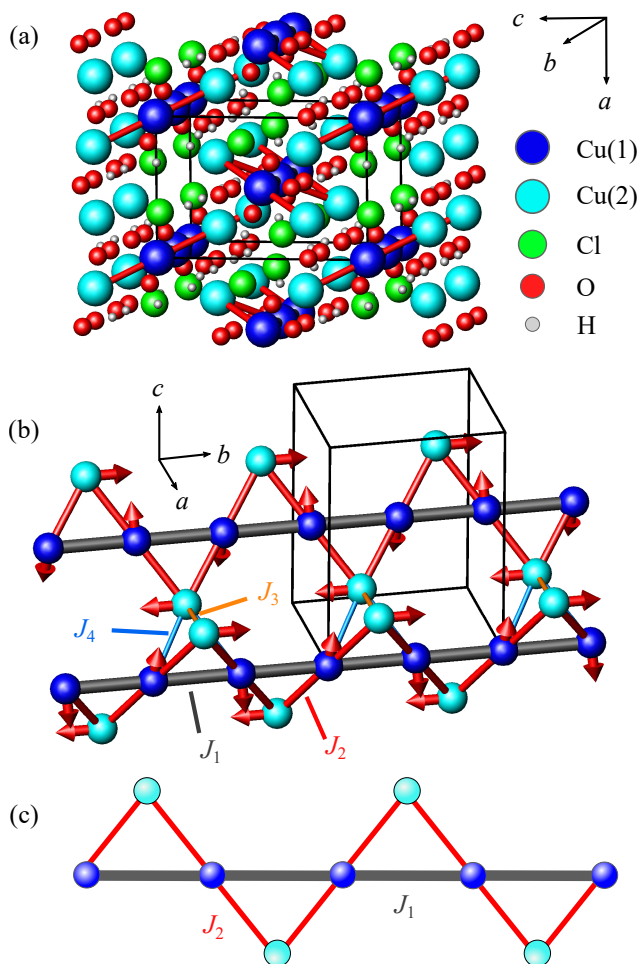


FIG. 1: (color online) (a) Orthorhombic crystal structure of atacamite $\text{Cu}_2\text{Cl}(\text{OH})_3$. (b) Visualization of the dominant magnetic exchange paths in atacamite, forming a sawtooth pattern, and the magnetic structure determined by neutron diffraction; for details see text. (c) Schematic drawing of the sawtooth chain model.

U (eV)	J_1 (K)	J_2 (K)	J_3 (K)	J_4 (K)
6	120.6(5)	38.4(3)	10.6(4)	-0.9(3)
7	103.1(3)	33.0(2)	5.5(3)	-1.7(2)
8	87.5(2)	26.5(2)	1.5(2)	-2.3(2)

TABLE I: The magnetic coupling strengths of atacamite $\text{Cu}_2\text{Cl}(\text{OH})_3$ obtained from band structure calculations. Couplings are given with respect to unit moments; for details see text.

appears (Fig. 1 (b) and (c)), with a dominant chain coupling $J_1 \sim 100$ K and the triangular coupling $J_2 \sim 30$ K. Chains at the edge and the center of the unit cell are canted with respect to each other, and are weakly magnetically coupled through exchanges J_3 and J_4 .

Strictly speaking, the lack of inversion symmetry between Cu(1)-Cu(1) and Cu(1)-Cu(2) pairs and the canting of neighboring chains would require the inclusion of a Dzyaloshinskii-Moriya interaction (DMI) and a staggering of the g -tensor in the magnetic model. Yet, these are secondary effects, where the DM interaction effectively leads to a magnetic exchange anisotropy of the order of a few K, while the g -tensor mostly affects the magnetic anisotropy in applied fields. On a temperature and field scale above ~ 10 K and ~ 10 T the magnetic behavior will be governed essentially by the couplings J_1 and J_2 , where we expect atacamite to behave as a $S = 1/2$ sawtooth chain. Only on the lowest energy scales of a few K and T the effects of 3D magnetic coupling should become relevant in form of long-range magnetic order in a frustrated magnet. To prove this, we have carried out a detailed experimental study of the magnetic ground state and the high-field behavior of single crystalline atacamite.

In our study, we have established the magnetic phase diagram of single crystalline atacamite using various techniques [39]. The magnetically ordered phase has been investigated by thermodynamics and neutron diffraction in zero and applied fields. For the thermodynamic investigation, we have carried out magnetization, susceptibility and specific heat measurements in fields up to 13 T using a commercial PPMS and a SQUID magnetometer (Quantum Design (R)). The neutron diffraction experiments have been performed at the Berlin Neutron Scattering Center, using the diffractometers E2 [44] and E5, in fields up to 6.5 T (first results in Ref. [45]). Aside from the determination of the magnetic structure, we have characterized the crystallographic structure of our natural single crystalline specimen atacamite [39, 46–48]. In addition, we have performed a high field (up to 65 T) magnetostriction and magnetization study at the Pulsed Field Facility of the National High Magnetic Field Lab. in Los Alamos to characterize the physical behavior beyond the magnetically ordered phase. In the present work, we will discuss only the data taken for magnetic fields H applied along the crystallographic b axis. A full

account of our study, including the data for the other crystallographic directions, will be given elsewhere [49].

Magnetic order in atacamite has been reported previously, although the microscopic details of the ordered phase had not been resolved [38, 40, 41, 45]. In our specific heat data in zero magnetic field, here plotted as c_p/T vs. T , we find a pronounced anomaly denoting a magnetic transition at $T_N = 8.4$ K (Fig. 2 (a)). As well, in the susceptibility in a low field of 0.1 T an antiferromagnetic (AFM) anomaly is observed at $T_N = 8.4$ K (derived from the criterion $d(\chi T)/dT = \max$; Fig. 2 (b)). In our neutron diffraction experiments we also find additional magnetic intensity with an ordering vector $\mathbf{q} = (1/2 \ 0 \ 1/2)$ (Fig. 2 (c)), although the transition temperature in zero field appears slightly higher with $T_N = 8.9$ K. The cause for this discrepancy is unclear.

In the specific heat, aside from the transition at T_N ,

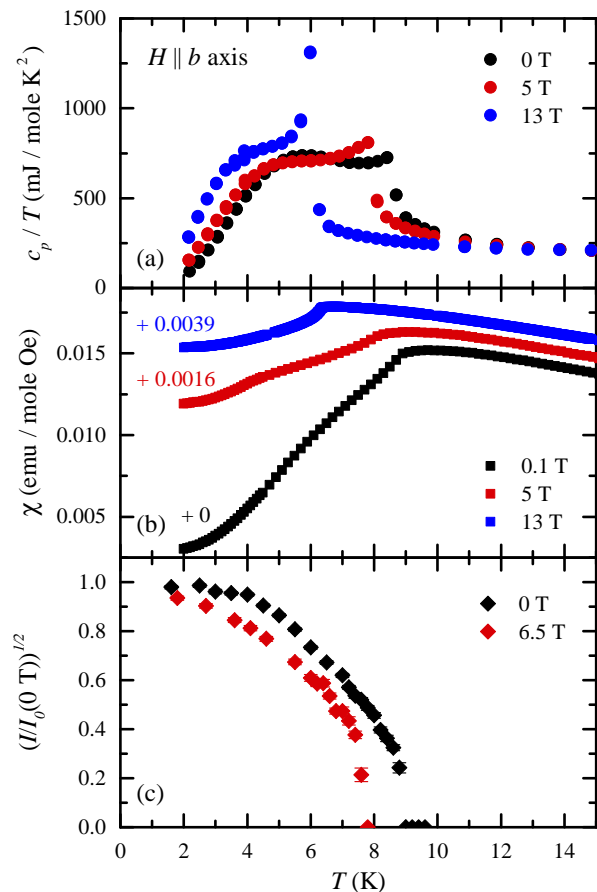


FIG. 2: (color online) Specific heat c_p/T (a), susceptibility χ (b) and normalized neutron scattering intensity of the $(1/2 \ 0 \ 1/2)$ peak (c) of atacamite $\text{Cu}_2\text{Cl}(\text{OH})_3$ in low/zero field and 13/6.5 T as function of temperature; all fields have been applied along the b axis. The susceptibility data have been shifted with respect to each other for clarity by the values denoted in the plot; for details see text.

there is an additional hump at lower temperatures ~ 5 K, hinting at a more complex temperature evolution of the magnetic state involving for instance spin reorientation effects. Still, calculating the entropy of the magnetic phase from our data (here ignoring the phonon contribution to c_p), it adds up to about $0.65R \ln(2)$ at T_N . Such a small value is typical for magnetically ordered states in frustrated magnets, with the magnetic entropy being distributed over the temperature scale set by the dominant coupling strengths, here J_1 and J_2 .

A magnetic field of 13 T applied along the b axis shifts the features in the specific heat to lower temperatures, and sharpens the anomaly at the magnetic transition at $T_N = 6$ K. Similarly, in the susceptibility we find the antiferromagnetic transition shifted to $T_N = 6.3$ K, while in the neutron diffraction experiment a field of 6.5 T moves T_N to 7.7 K. Altogether, an external magnetic field leads to the typical suppression of the AFM phase in atacamite, with the AFM transition estimated to be suppressed to zero temperature in the 20 T-range.

We note the difference in the susceptibility below T_N at low and high fields. For the latter, the absolute values of χ are much larger than in low fields. It reflects that a metamagnetic transition occurs at a few T, as established by magnetization measurements (see below). Since for the other crystallographic directions we find no metamagnetic transitions, it suggests that the b axis is essentially the easy magnetic axis and therefore the metamagnetic transition is a type of spin flop (see Supplemental Material [39]). This conclusion is consistent with our neutron diffraction study of the magnetically ordered phase. Here, we have determined the intensities of the magnetic Bragg peaks. From the analysis of these data we derive a magnetic structure as shown in Fig. 1 (b) (see Supplemental Material [39, 50]). On the Cu(1) site, ordered magnetic moments of $0.34(4) \mu_B$ are arranged in a canted antiferromagnetic pattern (components along the crystal axes $\mu_{\text{ord}}(a, b, c) = (0.09, 0.04, 0.32) \mu_B$). On the Cu(2) site one finds an antiferromagnetic alignment of ordered magnetic moments of $0.59(2) \mu_B$ along the sawtooth chain with the moment having a b component only.

To complete our study, we have carried out both magnetostriction and magnetization experiments in pulsed magnetic fields for $H \parallel b$ axis (for experimental details see Refs. [51, 52]). In Fig. 3 (a) we summarize the results of the magnetostriction experiments, in Fig. 3 (b) we present the corresponding magnetization data. At low temperatures and in fields up to ~ 6 T shallow minima in the magnetostriction denote the metamagnetic transition [39]. It then rises in a parabolic fashion up to ~ 31.5 T, where a sharp kink occurs and the magnetostriction is flattening off. Increasing temperature hardly affects the position of the kink, but smears out the feature until at 6 K no distinct kink is observable anymore.

The magnetization measurement confirms and reinforces the conclusions from the magnetostriction: At

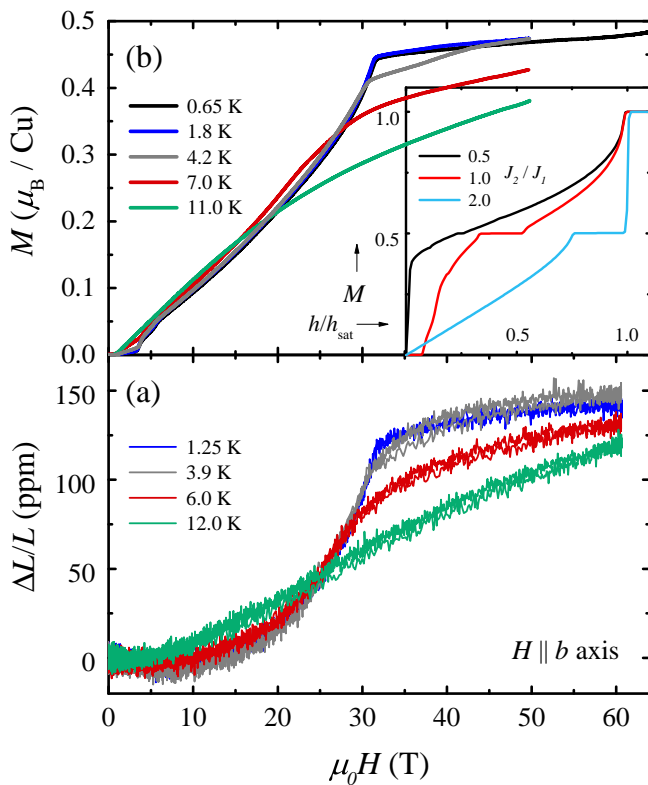


FIG. 3: (color online) (a) Magnetostriction and (b) magnetization of atacamite in pulsed magnetic fields $H \parallel b$ axis at different temperatures. The inset depicts the result of numerical calculations of the magnetization for the bare sawtooth chain and ratios J_2/J_1 denoted in the figure. Note that the pulsed field magnetization is calibrated by the 13 T PPMS VSM data; for details see text.

lowest temperatures and low fields the magnetization is rather small, but starts to rise at a few T due to a metamagnetic transition [39]. Beyond the metamagnetic transition the magnetization evolves with a slight upward curvature up to a magnetic field of 31.5 T, where a wide magnetization plateau at half of the full magnetization of the Cu^{2+} ions sets in. The plateau reaches up to highest measured fields. Its position is hardly temperature dependent but smears out significantly with temperature.

From our data we can now construct the magnetic phase diagram of atacamite for $H \parallel b$ axis (Fig. 4). From the figure, it can be seen that below T_N and in comparatively low fields up to 20 T there is the antiferromagnetic phase. It is further separated into a low-field regime with a magnetic structure described above, and the phase range beyond the metamagnetic transition, where a spin-flop transition occurs. After suppression of the AFM order, however, the system is still far from magnetic saturation. Instead, at 31.5 T a wide magnetization plateau at half of the full magnetization, *i.e.*, at $M_{\text{sat}}/2$, sets in. This type of magnetization plateau is known to exist for the sawtooth chain [24, 26]. Full magnetic saturation is

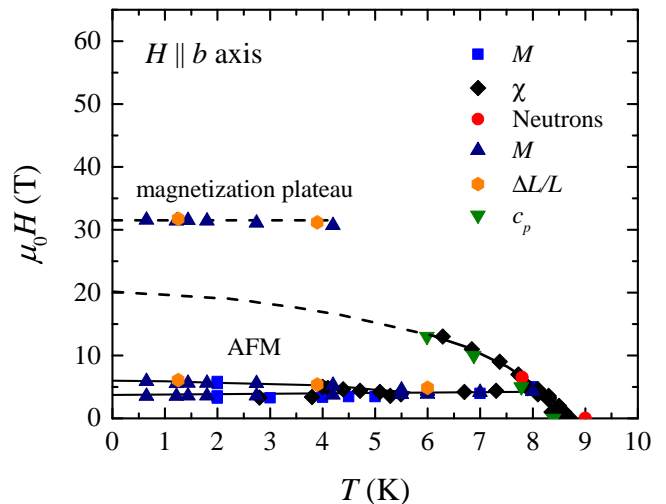


FIG. 4: Magnetic phase diagram of atacamite $\text{Cu}_2\text{Cl}(\text{OH})_3$ for $H \parallel b$; for details see text.

not reached at highest fields of 65 T.

Now we revisit the theoretical analysis of the magnetization plateau, carrying out zero-temperature infinite system time-evolving block decimation (iTEBD) calculations [53] as well as Lanczos diagonalizations. The inset of Fig. 3 exemplifies the magnetization from iTEBD at $J_2/J_1 = 2, 1$, and 0.5 . Several distinct features arise. First, a plateau occurs at $M_{\text{sat}}/2$ for $h_1 < h < h_2$. Second, the size of the plateau depends rather nonlinearly on J_2/J_1 , decreasing rapidly for small J_2/J_1 , where $M(h)|_{J_2/J_1=0} - 1/2$ has to comply with the Heisenberg chain. For the parameters we considered, the maximum size of the plateau occurs at $J_2/J_1 = 2$, decreasing again above that, with $M(h)|_{J_2/J_1 \rightarrow \infty}$ being twice that of the Heisenberg chain. Third, the sign of the curvature of $M(h < h_1)$ depends on J_2/J_1 . Finally, at $J_2/J_1 = 2$ the transition from full magnetization to the plateau exhibits a jump, attributed to flat magnon bands [26].

These results should be compared with our electronic structure calculations and experimental findings. The former provide clear evidence for a strongly 1D system, *i.e.*, $J_3 \lesssim 0.08J_1$, and $J_2/J_1 \approx 1/3$ (see Tab. I). The latter show a plateau at $M_{\text{sat}}/2$, extending over a sizable portion of the anticipated saturation field range (order of 100 T) and an upward curvature of $M(h)$ preceding the plateau. For a *bare* sawtooth chain, *i.e.*, the inset of Fig. 3, the latter two points suggest that $J_2/J_1 > 1$. This indicates, that a significant renormalization of J_2/J_1 has to occur beyond our current analysis. While we do not have a definite answer, there are several options. First, we have attempted to include additional magnetic couplings as for instance a frustrated next-nearest-neighbor exchange along the chain axis. However, these tend to suppress plateau physics [39]. Second, the calculated plateau is flat. Yet, in our experiment the plateau has

a small nonzero slope. This may indicate effects of finite Dzyaloshinskii-Moriya interactions and on-plateau canting of magnetic moments, which need to be aligned. Finally, it is conceivable that magnetic anisotropy enables a stabilization of a plateau phase. In the future, it would be interesting to investigate the role of the small 3D couplings J_3 and J_4 .

Our data shows that for atacamite the magnetic anisotropy is important to the material properties [54]. For example, the magnetic field at the onset of the magnetization plateau varies from 21 T along the c axis to 35 T along the a axis (not shown [49]). Moreover, we observe evidence of a spin flop in the magnetization for magnetic fields along b . Analyzing the DMI and local environments of the Cu(1) and Cu(2) sites in atacamite remains a task for future experimental and theoretical exploration.

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