Experimental report

13/05/2022

Proposal: **5-31-2864** **Council:** 4/2021

Title: Determining the intermediate-temperature incommensurate magnetic structure of antlerite

Research area: Physics

This proposal is a resubmission of 5-31-2828

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Samples: $Cu_3(OD)_4SO_4$

Instrument	Requested days	Allocated days	From	To
D20	2	2	21/06/2021	23/06/2021

Abstract:

The spin-1/2 quantum magnet $Cu_3(OH)_4SO_4$, isostructural to the natural mineral antlerite, is a one-dimensional compound with two nonequivalent copper sites, arranged into triple chains. While it was initially thought that one of the Cu spins shows idle-spin behavior, more recent experiments uncovered a complex magnetic phase diagram with multiple field-induced magnetic phases and various metamagnetic transitions. This motivated us to study this compound in more detail as a strongly frustrated low-dimensional quantum-spin magnetic system. In our group, we could synthesize large amounts of antlerite in the form of tiny single crystals or powder, which have been already measured at ANSTO and at D1B, ILL. While we have detailed temperature maps that demonstrate the presence of at least one metamagnetic phase transition from a commensurate to incommensurate magnetic phase, the lack of sufficient measurement time did not allow us to measure data with sufficient statistics to refine the magnetic structure. We therefore apply for a continuation experiment to complete the measurements.

Experiment Title

Determining the intermediate-temperature incommensurate magnetic structure of antlerite

Proposer

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Report

Experimental configuration and results

Our deuterated antlerite powder was measured on 21—23 June 2021, in vanadium can on D20 - High-intensity two-axis diffractometer with variable resolution at ILL, France. Neutron with the wavelength $\lambda = 2.41$ Å were selected using Germanium monochromator for higher take-off angles. We are interested in temperature range 4.5—5.8 K, based on the recent magnetic phase diagram [1], and good temperature stability was crucial for our experiment since some phases are very narrow in temperature. Neutron powder diffraction data in the paramagnetic phase are consistent with the Pnma space group with cell parameters $a = 8.208(3)$ Å, $b = 6.033(2)$ Å, $c = 11.954(7)$ Å, in good agreement with previous work [2–4].

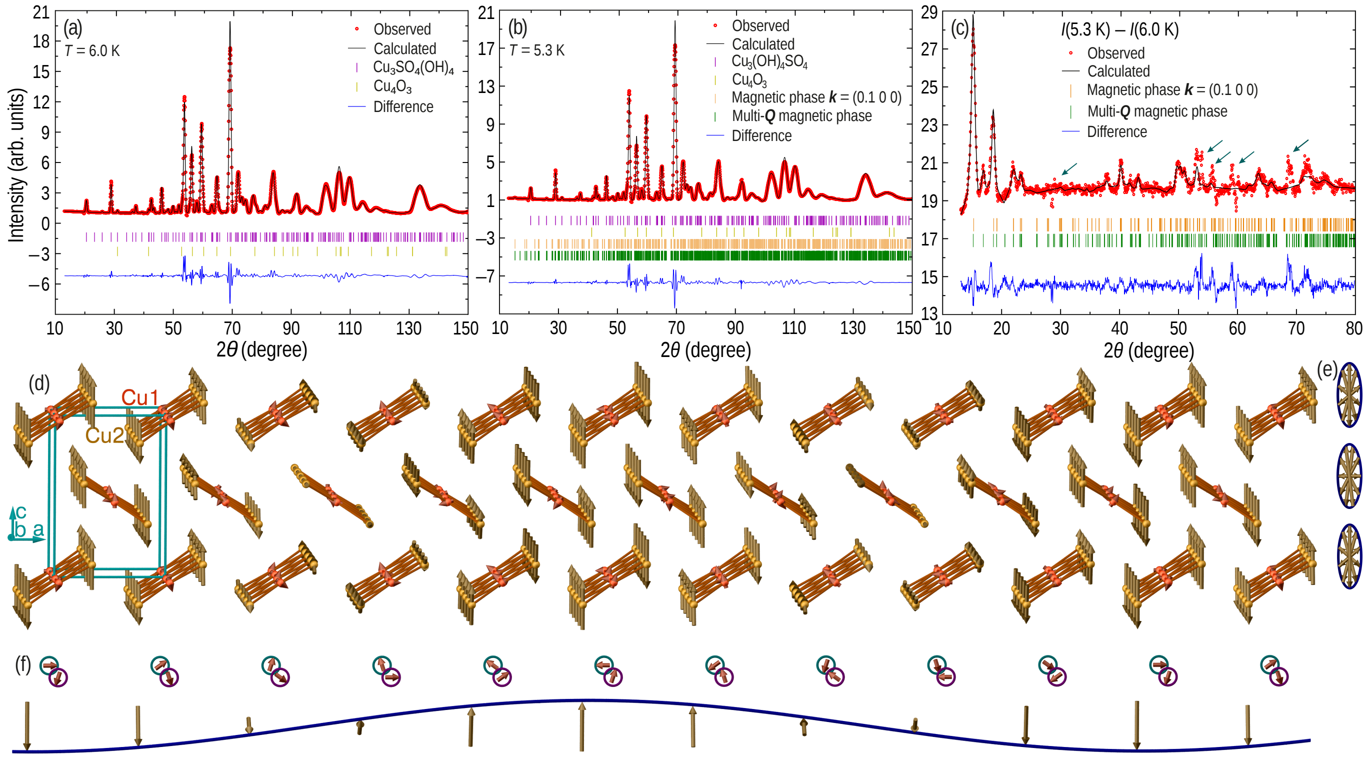

Fig. 1: Refinement of the incommensurate phase. Data are shown at (a) 6.0 K in the paramagnetic state and (b) 5.3 K where the incommensurate phase begins to yield to multiple-q order; their difference is plotted in (c). Arrows mark artifacts due to imperfect subtraction of strong nuclear peaks. The refined incommensurate order is shown in (d), and (e) shows a view along a of the elliptical helical order on the corner (upper and lower) and body-centered (middle) Cu2 ladders. The order pattern on selected Cu1 and Cu2 sites is shown in (f), using the same axes as in (d).

Data were first collected as a function of temperature to validate the thermometry, then for longer times at 6.0 K in the paramagnetic phase and at 5.3 K where the $(1\pm\delta\,0\,0)$ peaks reach their maximum intensity. Figure 1(a) shows the baseline data from D20 in the paramagnetic phase at 6.0 K, in Fig. 1(b) we present data at 5.3 K, and the difference between these two scans is shown in Fig. 1(c). This difference was refined to determine the magnetic structure. Since 5.3 K is on the cusp of the multiple-q phase, weak traces of the latter phase are visible, but the incommensurate peaks dominate. A contribution from the multiple-q phase was found to be present at the 1.3% level and was refined as discussed below.

Of the four possible magnetic irreducible representations, only Γ_2 gave an acceptable description of the magnetic intensity, but the unconstrained application of Γ_2 leads to physically unreasonable spin alignments on some ladders. If we constrain the Cu2 ordered moments to have equal magnitude on any given ladder, with spins on opposite legs exactly antialigned as in the lowest-temperature phase, and allow only one angle between consecutive spins on the central legs, a physically plausible magnetic model is obtained which leads to a minor improvement in the quality of the refinement. As shown in Fig. 1(d), the incommensurate phase corresponds to elliptical-helical order of the antialigned ferromagnetic spins on the outer Cu2 legs of the ladder paired with cycloidal order on the inner Cu1 leg. The helical and cycloidal order on selected Cu sites are also shown separately in Figs. 1(f), and a view of the elliptical order along the a axis is shown in Fig. 1(e). The propagation vector in this phase is $(\delta\,0\,0)$, where $\delta \approx 0.1$ at 5.3 K. The elliptical helix on the outer legs has major and minor axes of 0.41(4) and 0.15(8) μ_B while the cycloidal ordered moment on the central leg is 0.09(7) μ_B. These are small fractions of the full 1 μ_B moment, but it is also important to note that these refinements are performed on data collected at ~95% of T_N, where one would not ordinarily expect fully ordered moments. The angle between adjacent spins along the central leg refines to 108(40)°, likely due to a competition between nearest-neighbor and next-nearest neighbors along the leg, combined with the exchanges to the outer legs.

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