Experimental report

14/09/2021

Proposal: 5-41-1097 **Council:** 4/2020

Title: Magnetic order in natural brochantite

Research area: Physics

This proposal is a new proposal

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Samples: Cu4SO4(OH)6

Instrument	Requested days	Allocated days	From	To
D10	12	0		
D19	4	0		
D9	6	6	15/09/2020	21/09/2020

Abstract:

We propose to investigate magnetic order in natural mineral brochantite, chemical formula Cu4SO4(OH)6, by means of single crystal neutron diffraction. Brochantite belongs to S=1/2 geometrically frustrated two-dimensional (2D) Heisenberg quantum kagome antiferromagnets. Previous measurements on a synthetic polycrystalline sample showed that it orders below 7 K with a canted AFM structure as a result of competition of FM and AFM exchange interactions between strongly reduced Cu-moments. Our bulk characterization of the single crystal points to short-range low-dimensional antiferromagnetic behavior at higher temperatures with the consequent long-range magnetic order at low temperatures, as well as metamagnetic behavior in high-fields. We propose a single crystal diffraction experiment to determine the magnetic ground state of this spin-1/2 quantum system.

Experimental report: Crystal structure of natural brochantite at low temperatures

Introduction:

The intense search for quantum spin liquid (QSL) candidates revealed that the newly synthesized sulfate compounds with a chemical formula $Cu_4SO_4(OH)_6$ (synthetic analog of natural brochantite) and $ZnCu_3(OH)_6SO_4$ (so called Zn-brochantite) could be geometrically frustrated two-dimensional (2D) Heisenberg quantum kagome antiferromagnets [1-4]. The natural brochantite crystallizes in the monoclinic cell, space group $P2_1/a$ (14), and the key feature of the structure is the presence of edge-shared copper octahedra, giving rise to well magnetically separated corrugated 2D planes [5]. The investigation of a magnetic component of the heat capacity of natural $Cu_4SO_4(OH)_6$ suggests a gradual ordering of Cu magnetic moments from the 1D to the 3D state below $T_N \sim 7.5$ K [6]. The presence of geometrically frustrated Cu^{2+} (S = 1/2) magnetic sublattices turns such a system to a quantum magnet that can exhibit emergent phenomena and promotes exotic magnetic states at low temperatures.

Preliminary Results:

In the current proposal we were granted beamtime for investigations of crystal structure of natural brochantite single crystals at low temperatures. The neutron diffraction experiment at 2 K, 12 K and at room temperature (RT) has been performed using hot neutron single crystal diffractometer D9 operated with the wavelength of $\lambda = 0.837$ Å. In total, we have recorded 496 Bragg reflections at 2 K, 709 at 12 K, and 147 reflections at RT were collected as reference. In addition, the reciprocal space survey at 15 K and 1.5 K has been carried out using Laue diffraction on Cyclops instrument [7].

The summary of the results is provided below. In agreement with the Laue data we found that the sample demonstrates features of order-disorder structure, i.e. the layered structure where the layers can be arranged in different ordered or disordered ways [8]. Indeed, the measured reflections are significantly extended in the *a**-direction (see Fig. 1) and exhibit a double peak structure reflecting (100) twinning [8].

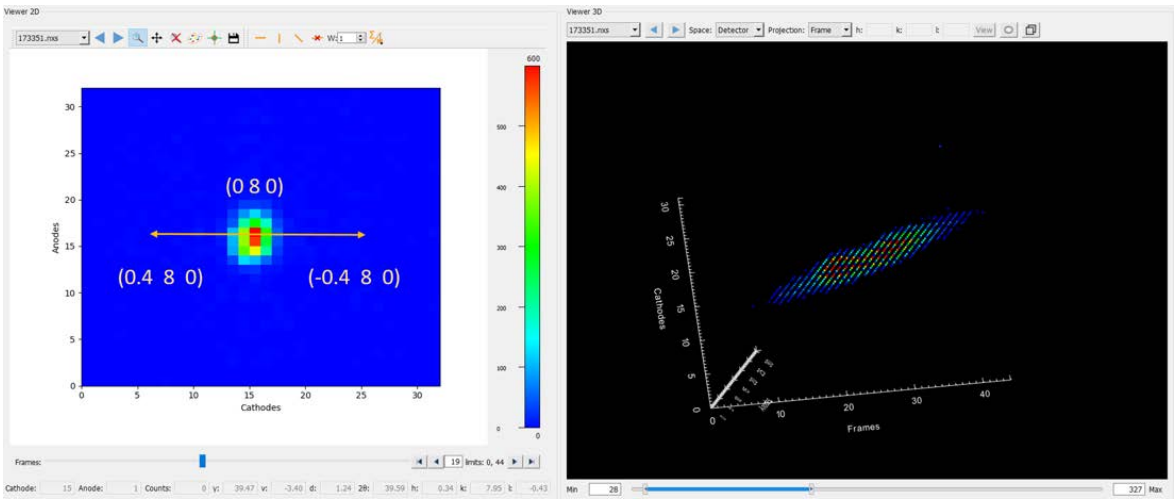

Fig. 1. A snapshot of the Bragg peak (0 8 0) showing the extension in the a* direction. During the omega-scans the reflections move in the direction of a* line that corresponds to a change in *h* of almost one reciprocal lattice unit.

The recorded data were used for the refinement of the crystal structure of the brochantite mineral (Fig. 2). Here an averaged structure has been treated, i.e. the intensity of both twins was integrated and the disorder has not been considered. A preliminary analysis using FullProf suggests that

the space group $P2_1/a$ (14) can describe the structure measured both at 12 K and 2 K. Below are the results of the refinement of the structural parameters of brochantite measured at 12 K. All the atoms were refined with isotropic displacement parameters. The anisotropic refinement has not provided reliable results.

Table I: Results of the crystal structure refinement at 12 K

Atomic coordinates			
atom	**x**	**y**	**z**
Cu_1	0.28783(69)	0.49159(88)	0.52015(155)
Cu_2	0.30309(66)	0.48896(83)	0.02610(141)
Cu_3	0.11641(87)	0.26029(74)	0.18271(150)
Cu_4	0.12151(99)	0.25691(89)	0.68611(187)
S	0.37850(199)	0.19704(189)	0.31124(405)
O_1	0.09249(126)	0.13373(117)	0.42208(256)
O_2	0.08358(136)	0.13354(122)	0.91669(246)
O_3	0.15499(119)	0.38077(113)	0.45306(232)
O_4	0.15768(121)	0.38760(118)	0.95321(227)
O_5	0.24159(101)	0.59851(97)	0.24584(183)
O_6	0.35932(102)	0.39980(111)	0.80815(246)
O_7	0.27585(109)	0.14637(124)	0.26391(228)
O_8	0.38394(117)	0.35652(139)	0.31602(275)
O_9	0.45066(133)	0.14780(126)	0.15357(259)
O_{10}	0.43593(130)	0.15206(135)	0.54598(264)
H_1	0.00630(212)	0.11706(213)	0.37585(489)
H_2	0.01735(241)	0.09735(246)	0.88490(511)
H_3	0.10491(196)	0.45665(198)	0.41376(346)
H_4	0.10705(251)	0.46030(268)	0.93801(461)
H_5	0.16422(255)	0.59539(264)	0.20749(641)
H_6	0.34430(213)	0.29408(244)	0.81358(513)
Lattice parameters	a = 13.122 Å b = 9.856 Å c = 6.036 Å β = 103.83°		
R- factors	R_{F2}= 17.3%		

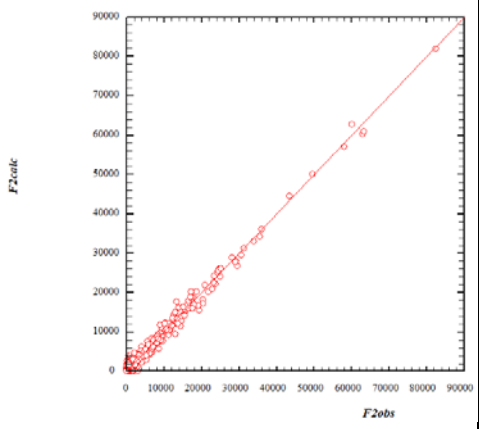

Fig.2. Observed vs. calculated structure factors squared obtained from the 12 K data refinement.

In agreement with the Cyclops data, we found no additional (magnetic) reflections appearing below the magnetic transition at 7.5 K. Several Q-scans have not shown any features below T_N. Comparing

the intensities of the nuclear peaks, however, one can identify a few of them, e.g. (1,2,0), (-4,0,1), (5,4,0), (0,6,1), which show significant increase at 2 K as compared to the 15 K data. This allows us to conclude that the magnetic contribution is located on top of the nuclear peaks, i.e. the magnetic propagation vector Q_{mag}=(0,0,0). This is in agreement with the results obtained by neutron powder diffraction on the synthetic sample [1]. Further investigations of the magnetic order in brochantite mineral will be performed on D10 single crystal diffractometer.

References: [1] S. Vilminot, et al. Dalton Trans. 1455 (2006); [2] Yuesheng Li, et al. New J. Phys. 16 093011 (2014); [3] M. Gomilšek, et al. Phys. Rev. B 93, 060405(R) (2016); [4] M. Gomilšek, et al. Phys. Rev. Lett. 119, 137205 (2017); [5] M. Helliwell and J.V. Smith, Acta Cryst. C53, 1369 (1997); [6] M. R. Bissengaliyeva et al., J. Chem. Eng. Data 58, 3904 (2013); [7] O. Prokhnenko, et al., Experimental report for proposal EASY-639; [8] see S. Merlino et al, Eur. J. Mineral. **15,** 267-275 **(**2003) and references therein