Experimental report

14/02/2020

Proposal: 5-24-645 **Council:** 10/2019

Title: A crystallographic study on the candidate quantum spin liquid ZnCu3(OD)6FCl

Research area: Physics

This proposal is a new proposal

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Samples: Cu4(OD)6FCl
ZnCu3(OD)6FCl

Instrument	Requested days	Allocated days	From	To
D2B	1	1	13/01/2020	14/01/2020

Abstract:

We propose to use neutron powder diffraction to study the crystal structure of the quantum (S=1/2) geometrically frustrated kagome material Zn-claringbullite, ZnCu_3(OD)_6FCl. This material is formed of a Cu^2+ kagome lattice and our room temperature structural refinements show it to crystallise in the P6_3/mmc space group, retaining the 3-fold symmetry of the kagome. We propose to use D2B to determine the Zn/Cu site occupancies, D atom site positions to characterise the Cu--OD--Cu magnetic superexchange pathways and identify any weak structural changes upon cooling.

Experimental report: $Zn_xCu_{4-x}(OD)_6FCl$ for $x = 0$ and 1 on D2B

1 Motivation

The aim of this experiment was to characterise the structures of the candidate quantum spin liquid (QSL) Zn-claringbullite, $ZnCu_3(OD)_6FCl$, and its parent material claringbullite $Cu_4(OD)_6FCl$ down to 1.5 K.

QSLs are exotic states of matter which are governed by global properties such as long-range entanglement and quasi-particle spinon excitations [1]. The experimental search for QSLs began when Anderson suggested they underpin the transition to unconventional superconductivity in the high-T_C cuprates [2]. The $S = \frac{1}{2}$ kagome Heisenberg magnet (KHM) is considered the most promising model system for the realisation of 2D QSLs. QSLs remain dynamic states of fluctuating spins at $T = 0$ K, so both their nuclear and magnetic structures must be determined at the lowest temperatures.

Experimental materials often show deviations from the ideal theoretical model, mainly due to ionic antisite disorder on the magnetic kagome lattice and crystallographic distortions. The antisite disorder is minimised in $ZnCu_3(OH)_6FCl$ due to the AAA stacking of the Cu kagome layers which stabilises the Zn position.[3] The structure is shown in Figure 1a.

We synthesised $ZnCu_3(OD)_6FCl$ and $Cu_4(OD)_6FCl$. Our laboratory powder x-ray diffraction (PXRD) measurements at 295 K showed both samples to crystallise in the $P6_3/mmc$ space group, in agreement with the literature [4]. Our dc magnetometry measurements on $ZnCu_3(OD)_6FCl$ showed no transition to long-range order down to 2 K and from the high-temperature region of $1/\chi$ we extrapolated $\theta_W = -261$ K (Figure 1b), in good agreement with the literature ($\theta_W = -223$ K) [4].

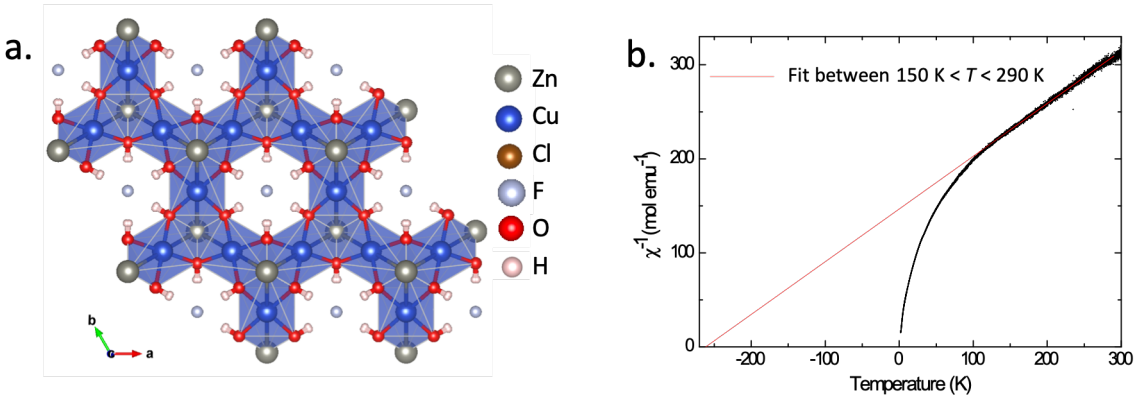

Figure 1: (a) Crystal structure of $ZnCu_3(OH)_6FCl$. (b) Magnetic susceptibility shows no sign of long-range magnetic order.

2 Aim of experiment

Neutron diffraction of $Zn_xCu_{4-x}(OD)_6FCl$ for $x = 0$ and 1 was carried out at temperatures between 1.5 K and 300 K to characterise:
1. The nuclear structure of $x = 0$ at room temperature including the location of the lighter O and D atoms.
2. The nuclear structure of $x = 0$ at 1.5 K as single crystal data showed some samples to undergo a crystallographic transition to $Pnma$ at 110 K whilst others remained hexagonal down to 10 K.[5] This called for further clarification of the low temperature structure as it seemed to be sample-dependant.
3. Explore whether $x = 1$ has a similar crystallographic transition.
4. Locate the Cu, Zn, O and D atomic positions in the $x = 1$ sample.

3 Measurements

Measurements were performed on D2B with $\lambda = 1.595238$ Å.
The sample cans used were 8.5 mm vanadium cans. Both samples were fully deuterated and we used 5.17 g of $Cu_4(OD)_6FCl$ and 3.60 g of $ZnCu_3(OD)_6FCl$. $Cu_4(OD)_6FCl$ was measured at 1.5 K and 300 K with s200 collimating slits for 4 h. $ZnCu_3(OD)_6FCl$ was measured at 300 K with the same collimating slits (4 h measurement). At 1.5 K and 50 K, additional 10' collimators were used and the data collections took 6 h. For the measurements below room temperature, the samples cans were placed in an orange cryostat.

4 Results

Powder diffraction patterns have initially been analysed using Pawley refinements. The $Cu_4(OD)_6FCl$ sample was verified to crystallize in the $P6_3/mmc$ at room temperature and $Pnma$ at 1.5 K. On the other hand, $ZnCu_3(OD)_6FCl$ remains in the $P6_3/mmc$ space group down to 1.5 K. A diffraction pattern with a Pawley refinement is shown in Figure 2.

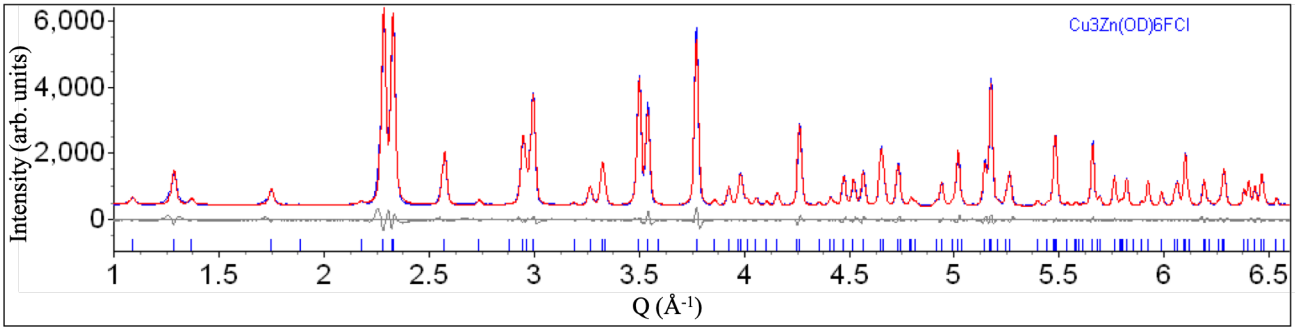

Figure 2: Initial Pawley refinement (red) of $ZnCu_3(OD)_6FCl$ neutron diffraction data (black) collected at 1.5 K. All peaks can be indexed in the $P6_3/mmc$ space group.

References

[1] Knolle, J. *et al.*, *Annu. Rev. Condens. Matter Phys.* **2019**, 10, 451.
[2] Anderson, P.W. *et al.*, *Phys. Rev. Lett.* **1987**, 58, 2790.
[3] Smaha, R.W. *et al.*, *J. Solid State Chem.* **2018**, 268, 123.
[4] Feng, Z. *et al.*, *Chin. Phys. Lett.* **2019**, 36, 017502.
[5] Henderson, A. *et al.*, *Chemical Communications* **2019**, 55, 11587.