

Experimental report

06/02/2025

Proposal: 5-31-2952

Council: 4/2023

Title: Magnetic Structure of Kagome In-Kapellasite, $\text{InCu}_3(\text{OD})_6\text{Cl}_3$

Research area: Physics

This proposal is a new proposal

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Samples: In-kapellasite
 $\text{CuSn}(\text{OD})_6$

Instrument	Requested days	Allocated days	From	To
D1B	3	3	07/12/2023	10/12/2023

Abstract:

In-kapellasite is a new synthetic member of the kapellasite family, hosting $S=1/2$ Cu^{2+} in kagome planes. It contains no Zn and no risk of cross-substitution, so its kagome lattice has relatively low disorder. At present the hydrogen positions are not fully known. The magnetization and specific heat indicate a change in behaviour around 7 K, followed by a sharp magnetic transition at 1.8 K. We propose to determine the H/D positions, the magnetic structure of the low-temperature magnetically ordered phase, whether the phase between 1.8 and 7 K supports long-range magnetic order, and what this order is if so. The ordered moment of Cu is extremely weak, so this requires high intensity and very long count times, and getting well below the 1.8 K transition may be important.

Experiment Title

Magnetic Structure of Kagome In-Kapellasite, $\text{InCu}_3(\text{OD})_6\text{Cl}_3$ (#5-31-2952)

Proposer

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Report

Introduction

The Sapporo group has recently prepared for the first time an In-kapellasite, $\text{InCu}_3(\text{OD})_6\text{Cl}_3$. It forms in the trigonal space group $P31m$ and contains two crystallographically distinct Cu^{2+} sites in a Kagome plane. Unlike the quantum spin liquid candidate herbertsmithite [1–3], In-kapellasite contains no Zn and does not support cross substitution between the Cu and another site, which would lead to disorder on the magnetic sublattice. Since In-kapellasite orders magnetically, a better comparison may be to Ca-kapellasite, $\text{CaCu}_3(\text{OD})_6\text{Cl}_2 \cdot 0.6\text{D}_2\text{O}$, whose ground state hosts gapless spin excitations and is thought to be close to a quantum critical point [4, 5]. The Cd analog does not order down to 0.7 K [6].

Experimental configuration and results

We have carried out a study on the D1B using high-intensity neutron powder diffraction to determine the magnetic phases. The measurement was performed at the Institut Laue-Langevin (ILL) in Grenoble, France, using a dilution fridge. The measurement was made from 0.77 to 128.67 degrees with a step of 0.1, using a 2.52 Å wavelength. The counting times were approximately 28 hours at 0.04, 4 and 20 K for each temperature. The wavelength was chosen by pyrolytic graphite (002).

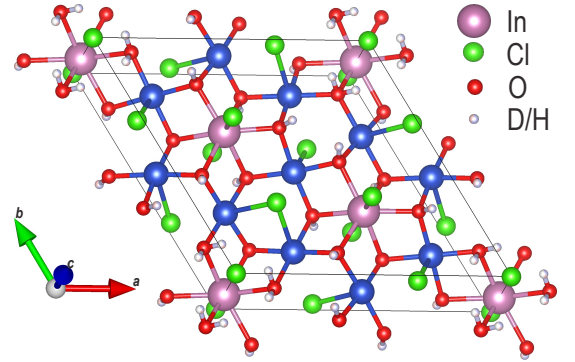


Fig. 1: Crystal structure of the In-kapellasite.

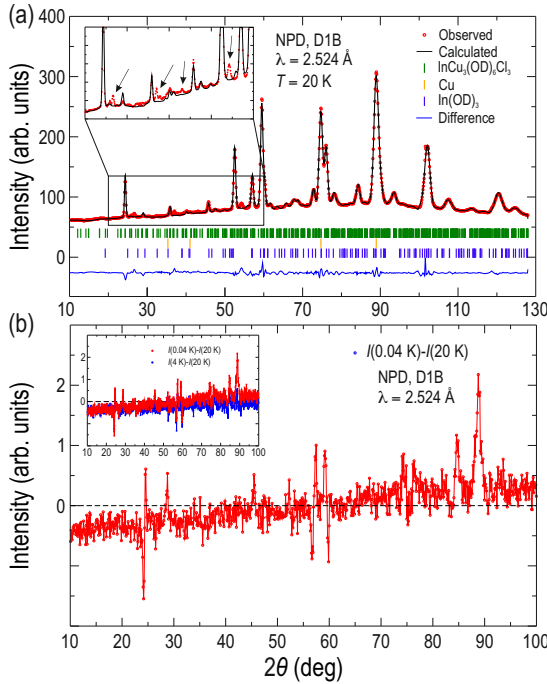


Fig. 2: (a) Scattered neutron intensities at 20 K as a function of 2θ , refined in the trigonal space group $P31m$ space group. Insert is zoom where black arrows indicate the peaks from undefined impurity. (b) Difference between the 0.04 and 20 K. Insert shows the difference between 0.04 and 20 K, 4 and 20 K.

The resulting crystal structure for In-kapellasite and refinements are shown in Fig. 1 and Table I. The refined atomic positions are given in Table II. The refined deuteration level is 63 %. The Rietveld refinement for the neutron powder diffraction data was performed in FULLPROF [7]. One deuterium/hydrogen position is shared, so that different oxygen sites have between two partially occupied deuterium/hydrogen sites to which they are covalently bonded, their total occupation adding up to one. Simultaneous occupation of any two sites bonded to the same oxygen is forbidden. The hydrogen bonding network in this case follows some analog of the ice rules.

Except for in-kapellasite, we found the same amount of $\text{In}(\text{OD})_3$ as an impurity phase. In addition, we found low intensity peaks at low angles that we cannot explain. We are inclined to believe that these are impurities because we observed them in the X-ray data. All these peaks are marked with black arrows in Fig. 2 (a) insert.

Long-range magnetic order and short-range magnetic correlation appear below 1.8 and 7 K, respectively, based on specific heat and magnetization data. We measured powder neutron diffraction at 0.04, 4 and 20 K. Sharp magnetic peaks appear at 0.04 K. It is shown as difference between 0.04 and 20 K datasets in Fig. 2 (b). There are two possible corresponding magnetic propagation wave vectors: $(\frac{1}{8} \frac{1}{4} \frac{1}{4})$ and $(\frac{1}{4} \frac{1}{8} \frac{1}{4})$. Irreducible representations analysis shows only one irreducible representation for our magnetic structure. But we still need to refine more than 20 parameters to solve the magnetic structure, which makes it impossible to find the magnetic structure with such a set of magnetic peaks in our data. Also we observe the decrease of the background at low angle, you can see it in Fig. 2 (b) insert, where differences between 0.04 and 20 K, 4 and 20 K datasets are shown.

There are no magnetic peaks at 4 K, probably because it is weak and we do not count long enough.

Table I: Unit cell parameters and R factors for our refinement of neutron diffraction data at $T=20$ K.

Parameters	InCu ₃ (OD) ₆ Cl ₃	In(OD) ₃
Wavelength (Å)	2.524	
Temperature (K)	20	
Space group:	$P31m$ (#157)	$Pmma$ (#51)
Ratio (%)	54	46
a (Å)	11.240(2)	7.943(7)
b (Å)	11.240(2)	3.182(8)
c (Å)	5.987(2)	5.035(3)
α	90	90
β	90	90
γ	120	90
V (Å) ³	655.0(3)	127.3(4)
R-Factor(%)	0.905	
Rp(%)	6.020	
Rwp(%)	5.310	

Table II: Refined atomic positions in synthetic InCu₃(OD)₆Cl₃ based on our neutron powder diffraction data at 20 K. Wy is the Wyckoff position.

Site	Wy	x	y	z	U	Occ.
In1	2b	0.33333	0.66667	0.59370	0.0	1.00
In2	1a	0.0	0.0	0.39850	0.0	1.00
Cu1	3c	0.50830	0.50830	0.52430	0.0	1.00
Cu2	6d	0.66667	0.83770	0.49630	0.0	1.00
Cl1	2b	0.33333	0.66667	0.00710	0.0	1.00
Cl2	3c	0.66100	0.66100	0.16750	0.0	1.00
Cl3	3c	0.32880	0.32880	0.84250	0.0	1.00
Cl4	1a	0.0	0.0	-0.00820	0.0	1.00
O1	6d	0.34260	0.49990	0.39400	0.0	1.00
O2	6d	0.53190	0.67530	0.66300	0.0	1.00
O3	3c	0.79830	0.0	0.33200	0.0	1.00
O4	3c	0.83130	0.83130	0.59400	0.0	1.00
D1	6d	0.32416	0.50789	0.21823	0.0	0.63
D2	6d	0.57453	0.68576	0.80766	0.0	0.63
D3	3c	0.79005	0.0	0.17560	0.0	0.63
D4	6d	0.88836	0.83198	0.70632	0.0	0.63
H1	6d	0.32416	0.50789	0.21823	0.0	0.37
H2	6d	0.57453	0.68576	0.80766	0.0	0.37
H3	3c	0.79005	0.0	0.17560	0.0	0.37
H4	6d	0.88836	0.83198	0.70632	0.0	0.37

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