Experimental report

14/09/2023

Proposal: EASY-1199 **Council:** 4/2023

Title: Vibrational spectrum of the proton network in the double hydroxide perovskite CuSn(OH)6

Research area: Physics

This proposal is a new proposal

Main proposer: Dmytro INOSOV

Experimental team:

Local contacts: Monica JIMENEZ RUIZ

Samples: CuSn(OH)6

Instrument	Requested days	Allocated days	From	To
IN1	6	6	31/08/2023	01/09/2023

Abstract:

This is a test measurement to test the feasibility of measuring the proton vibrational spectrum on Lagrange. We will use Lagrange to obtain the vibrational spectrum of the H..O-H bond network in the double hydroxide perovskite CuSn(OH)6. We succeeded in refining the structure of this compound including hydrogen positions for the first time. The material features correlated proton disorder governed by its own "ice rules", similar to that in water ice. The goal of the present experiment is to get an independent confirmation of the structure by extracting the OH bond lengths and hydrogen bond angles from the vibrational spectrum. We see this an an essential intermediate step in understanding the proton network, its disorder, dynamics, and ultimately the interplay with magnetism in a proton-disordered S=1/2 magnetic material. If our approach proves successful, other transition-metal hydroxide perovskites will be investigated in follow-up experiments.

Experimental report for proposal EASY-1199 (IN1)

After our proposal 7-01-588 was rejected, this short measurement was scheduled as a quick feasibility test to verify if one can use IN1-Lagrange to study the vibrational spectrum of hydrogen in double hydroxyperovskites, and if the resulting signal would be useful for verifying the structural model. A short measurement (∼6 h) has been conducted by the instrument scientist Monica Jimenez-Ruiz on the powder sample of protonated $CuSn(OH)_6$ with a mass of approximately 0.5 g. Later, the cubic $MnSn(OH)_6$ sample has also been measured as a reference. The experiment was performed on the neutron vibrational spectrometer IN1-Lagrange using the Cu (220) configuration that covers the energy transfer range from 20 to 500 meV. The data were taken at 5 K in order to decrease the Debye-Waller factor. A post-processing treatment of normalisation to monitor and subtraction of the empty cell was done using Mantid.

The resulting background-subtracted data are shown in Fig. 1 below. Despite the short measurement time, the data have enough statistics to see multiple peaks resulting from vibrational modes of the proton network. In Fig. 2 on the next page, we show the preliminary analysis of the $CuSn(OH)_6$ data, which is decomposed here into a sum of 25 individual Voigt peaks. The large number of peaks likely comes from the split hydrogen positions and the Jahn-Teller distorted crystal structure of $CuSn(OH)_6$ (mineral name: mushistonite). A more rigorous analysis of these data based on LDA calculations in collaboration with theorists is still ongoing.

We expect that these data should be already sufficient to confirm the structural model of mushistonite, which we previously obtained from a combination of neutron and x-ray diffraction. The difficulty is that every proton position appears to be split in the crystal structure, exhibiting correlated proton disorder. Combined with the low-symmetry unit cell with an orthorhombic distortion, this makes the refinement based on diffraction data alone highly challenging and prone to multiple solutions. We therefore intend to complement the Lagrange data with Raman measurements, which would be compared with the LDA calculations based on our structural model in order to get an independent verification of the proton network ordering.

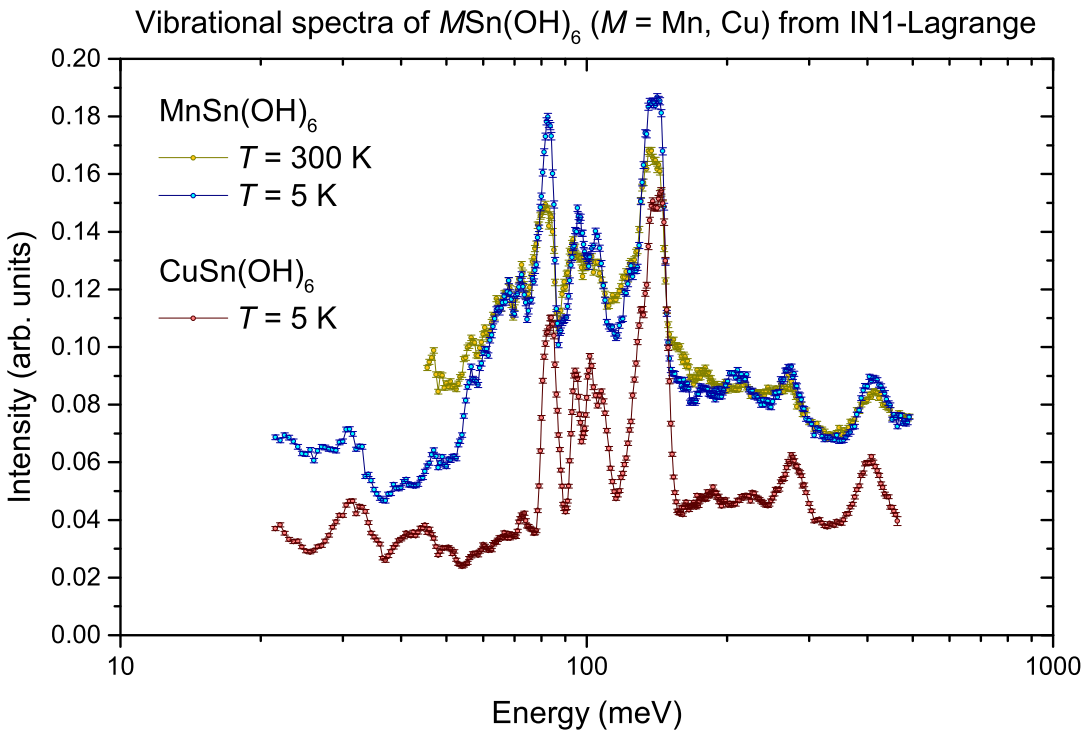

Fig. 1: Background-subtracted data measured on the two samples, $CuSn(OH)_6$ and $MnSn(OH)_6$, using the hot-neutron vibrational spectrometer IN1-Lagrange.

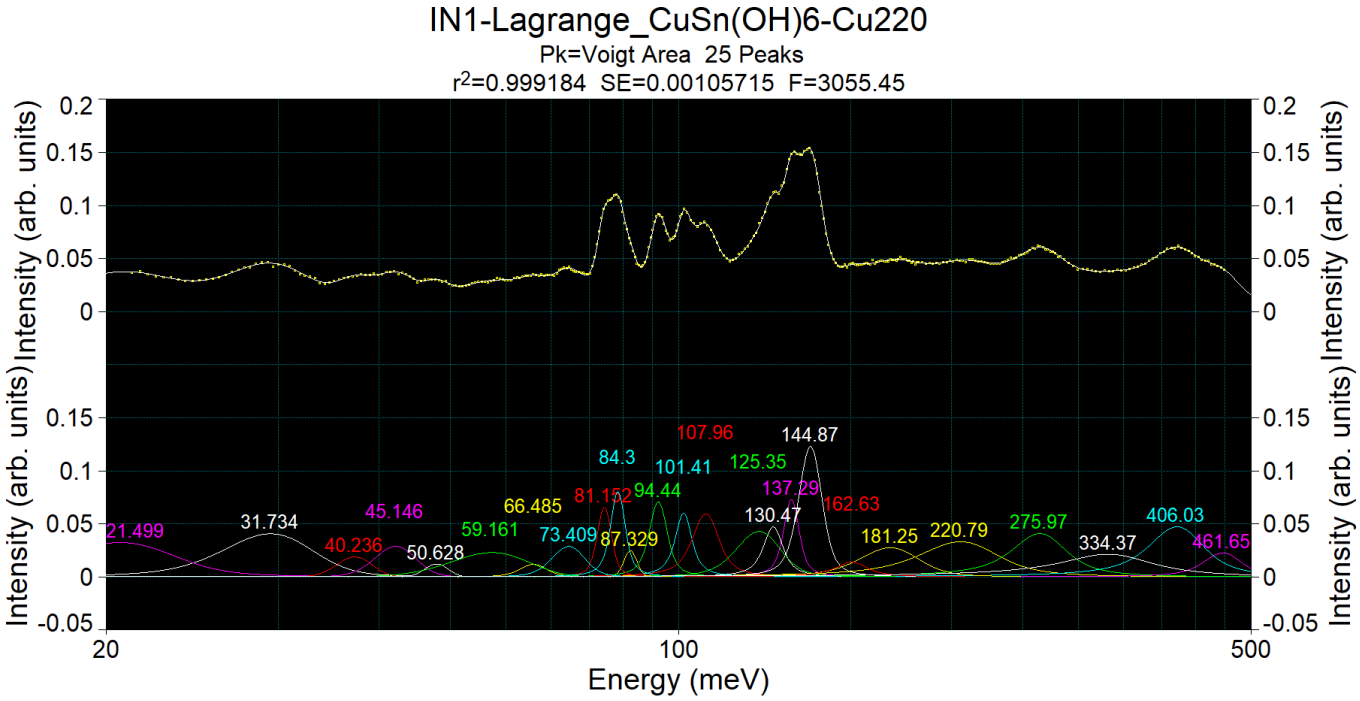

Fig. 2: The INS spectrum of $CuSn(OH)_6$ collected at $T = 5$ K on Lagrange (top) and its preliminary decomposition into a sum of Voigt peaks (white line). The individual peaks and their fitted positions are given below. A more thorough interpretation of these data in collaboration with theorists is now ongoing.