Experimental report

10/03/2024

Proposal:	**5-24-708**	**Council:**	4/2023
Title:	Proton disorder in the double hydroxide perovskite CuSn(OH)6 under hydrostatic pressure		
Research area:	Physics		

This proposal is a new proposal

Main proposer:	**Dmytro INOSOV**
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Samples: CuSn(OD)6

Instrument	Requested days	Allocated days	From	To
D20	7	3	08/09/2023	11/09/2023

Abstract:

We have identified a transition-metal hydroxide perovskite that combines correlated proton disorder with geometrically frustrated S=1/2 magnetism of Cu2+ ions. We expect that similarly to water ice, the proton network in CuSn(OH)6 may order under hydrostatic pressure. Therefore we are interested in measuring neutron diffraction under pressure in the Paris-Edinburgh cell up to ~5 GPa at temperatures down to ~80 K to look for structural changes in the proton network. Both deuterated and protonated phase-pure powder samples are already available. If any such changes are revealed, their influence on magnetic properties will be addressed in follow-up studies.

Experiment Title

Proton disorder in the double hydroxide perovskite $CuSn(OD)_6$ under hydrostatic pressure

Proposer

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Report

Introduction

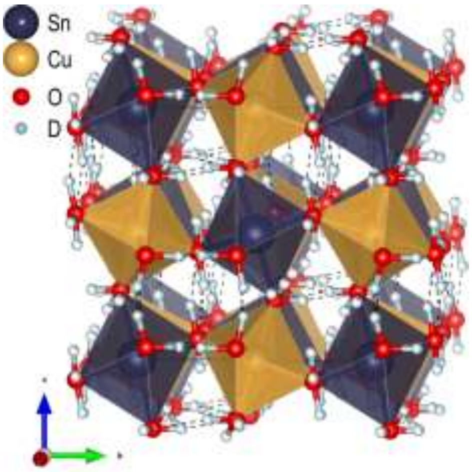

Fig. 1 The crystal structure of $CuSn(OD)_6$

Copper tin hydroxide $CuSn(OH)_6$ (mineral name: mushistonite [1]) is a rare example of a three-dimensional spin-½ system in which magnetic Cu^{2+} ions form a face-centered sublattice that serves as a playground for studying frustrated quantum-spin magnetism in 3D. On the other hand, this double perovskite represents an excellent model system for studying the interplay of magnetism and proton disorder [2]. From this perspective, it serves as a magnetic analogue of water, and we intended to study its structure as a function of pressure in a Paris-Edinburgh cell to search for possible structural phase transitions that could be related to proton ordering.

Experimental configuration and results

Our deuterated $CuSn(OD)_6$ powder was measured on 7–11 September, 2023, on the D20 high-intensity two-axis diffractometer at the ILL, France. Neutrons with the wavelength λ = 2.41 Å were selected using a Ge (113) monochromator. We mixed the powder with a small amount of Pb to establish a standard for determining on-sample pressure and its homogeneity. Afterward, we placed it in a Zr-Ti (null-scattering alloy) gasket inside the standard Paris-Edinburgh cell within a cryostat. We were interested in the temperature range of 80–300 K, and hydrostatic pressure up to 10 GPa in order to have high-statistic data in various points of the pressure-temperature diagram to refine complex unit cell with many free parameters.

One of the results of this experiment is the refinement of the crystal structure of this compound. It was discovered that instead of *P42/nnm*, initially proposed in 1976 [3], and contrary to the previously proposed *P2/n* structure, the correct space group is orthorhombic *Pnnn* (Fig. 1). In addition, neutron diffraction reveals strong disorder on

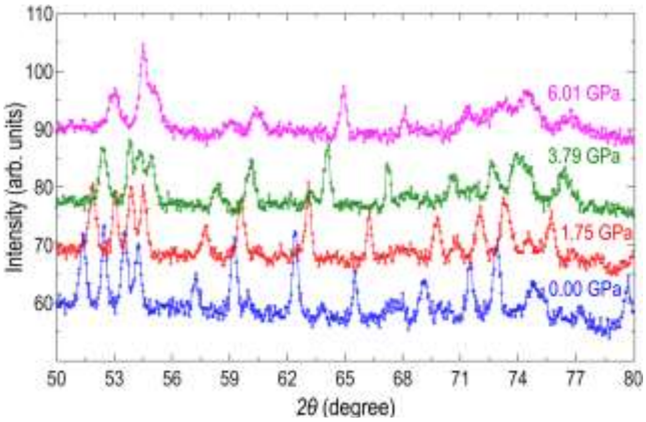

Fig. 2. A selection of diffraction patterns measured at different pressures.

all hydrogen or deuterium sites, similar to that previously reported for $MnSn(OH)_6$ [4]. As in the case of conventional water ice, each hydrogen atom statistically occupies one of two possible equilibrium sites. The occupation also follows nontrivial “ice rules”, namely that no two H/D sites facing each other or belonging to the same oxygen can be occupied simultaneously. This results in a disordered but highly correlated O· · ·O-H bond network. In $CuSn(OH)_6$ we have the same situation with pairs of equivalent hydrogen positions facing each other. In total there are 3 inequivalent positions for oxygen (O1, O2, O3) and 9 positions for hydrogen/deuterium (D12, D13, D23, D24, D21, D32, D33, D34, D35) which are all split at ambient pressure.

Selected distances between equivalent H/D sites are shown in Fig. 3. These distances were extracted from the refined crystal structures after processing the neutron data in the FullProf software [5]. Examples of fitting neutron powder data at different pressures and temperatures can be seen in Fig. 4. As pressure increases, the D34 and D35 sites bonded to the O3 oxygen first merge into a single split site, as shown in Fig. 3 (a). Simultaneously, the O1-D13 and O2-D23 bonds rotate, forming a hydrogen bond with another neighbour, as shown in Fig. 2 (b,c) respectively. In the case of the D12 site in Fig. 2 (a), the distance between the two equivalent sites facing each other is reduced but no merging occurs up to 7 GPa. Our measurement was interrupted at this pressure due to the rupture of the sample gasket (inset). By extrapolation, we estimate that the ordering transition on this site is expected at approximately 13-14 GPa.

We performed the measurements at several temperatures, but as one can see from Fig. 2, the atomic positions and bond angles do not show any significant temperature dependence. All the extracted distances between equivalent H/D sites only vary with temperature by no more than a few tenths of an Angstrom, which is within statistical uncertainty.

As can be seen from Fig. 3 (a), this experiment lacked data at higher pressures to reach proton-ordering transitions on more than just one proton site. During the transition from 7 GPa to approximately 9 GPa, the cell with the sample burst with a loss of pressure, and we did not have enough remaining time to reload the pressure cell. Therefore, a continuation proposal to complete our dataset with higher-pressure data is justified. The data available so far gives convincing evidence that

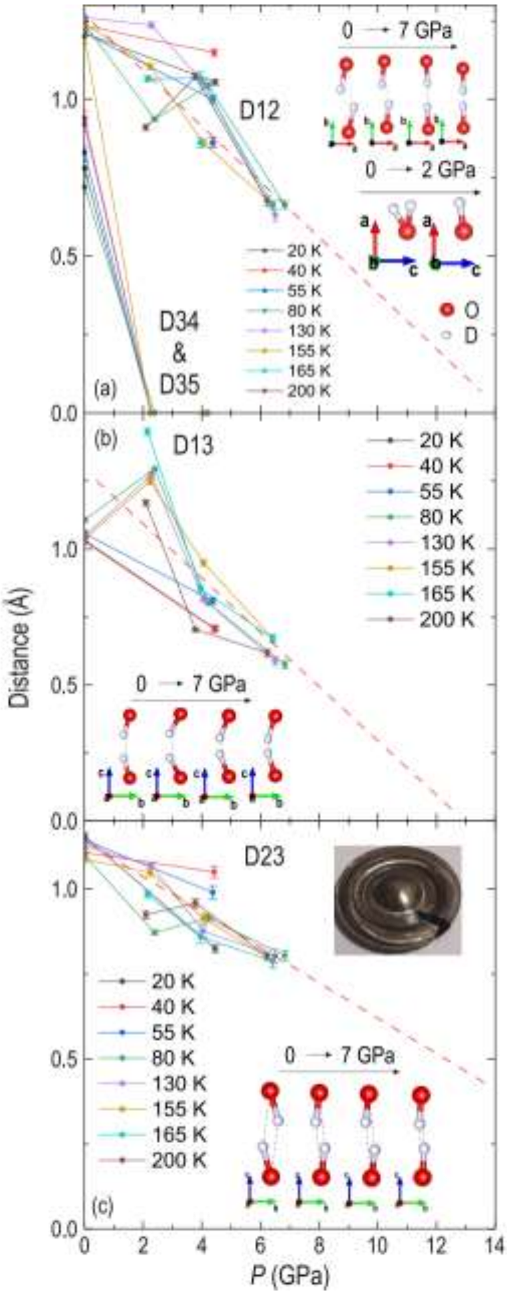

Fig. 3. Pressure dependence of the distances between some split H/D sites in the crystal structure of deuterated mushistonite $CuSn(OD)_6$, obtained from the preliminary refinement of our D20 data. The insets show the evolution in the geometry of the OH bonds.

hydrostatic pressure causes a whole cascade of proton-ordering transitions in hydroxide perovskites that deserves a closer investigation.

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[2] K. Komatsu *et al.*, Crystallogr. Rev. 28 224–297 (2022).
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[4] B. Lafuente, H. Yang, and R. T. Downs, Acta Cryst. A E71, 234–237 (2015).
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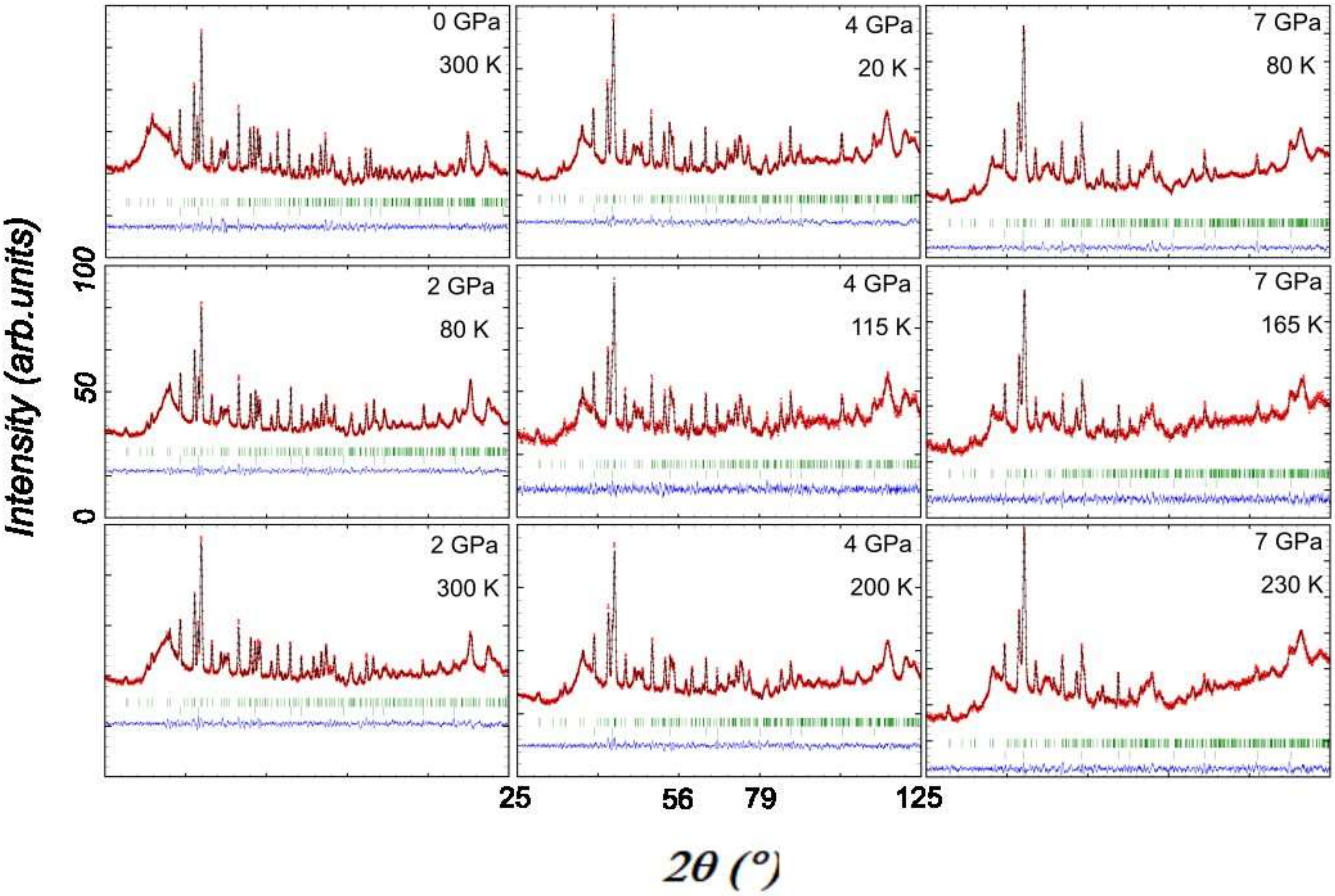

Fig. 4. Neutron powder diffraction data at different pressures and temperatures. **Red** – observed intensity; **black** – calculated intensity; **green** – peak positions; **blue** – residuals.