Supporting information

Neutron and X-ray Investigations of the Jahn-Teller Switch in Partially Deuterated Ammonium Copper Tutton Salt, $(NH_4)_2[Cu(H_2O)_6](SO_4)_2$

Authors

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S1. Phase fractions vs. pressure at additional temperatures

Included in the supplementary materials is the so-called "flat" file for the 60% deuterated sample, **d60**, at 295 K, "60D_295K.flt." This is an ASCII file with each line containing the two-theta value and then the intensity for each pressure step. These data are displayed in Figure 3 in the text of the paper using the program *2DFLT* [Yakovenko, A. A. (2014). 2D-FLT - In Situ Data Explorer], which can be downloaded from https://sourceforge.net/projects/twodflt/. Both the upper and lower figures in Figure 3 were obtained using the *2DFLT* program.

The Le Bail fits to the spectra were performed using the *JANA2006* program [Petříček, V., Dušek, M. & Palatinus, L. (2014). *Z. Kristallogr.* **229**, 345–352.]. Included in the supplementary materials are the *JANA2006* files for the **d60** mixed-phase same at 295 K and 50 bar (step 0):

60D_295K_50bar_mixed-phase_step0.m40
60D_295K_50bar_mixed-phase_step0.m41
60D_295K_50bar_mixed-phase_step0.m50
60D_295K_50bar_mixed-phase_step0.m90
60D_295K_50bar_mixed-phase_step0.m91
60D_295K_50bar_mixed-phase_step0.prf
60D_295K_50bar_mixed-phase_step0.ref

The Le Bail fit shown in Figure 4 can be reproduced with these files and *JANA2006*. The refinement log file 60D_295K_50bar_mixed-phase_step0.ref file provides a summary of the Le Bail refinement, including the unit cell parameters for each phase, the Gaussian and Lorentz parameters for the pseudo-Voigt profile function, and the agreement factors. The m91 file contains hkl (columns 1-3), the integrated intensity (column 7) and the phase number (column 11). These data were used in equation (1) given in the text to calculate the phase fractions.

Below are figures of phase fractions vs. pressure for of 291 K, 293 K and 200 K.

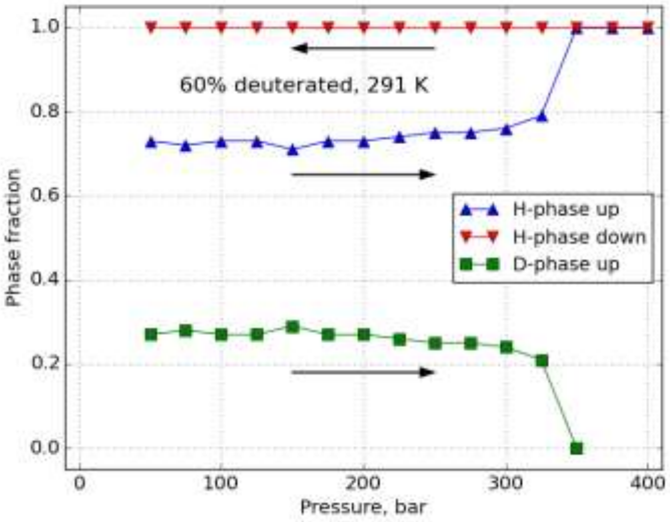

Figure S1 The phase fractions for the 60% deuterated (**d60**) sample at 291 K. This sample is already 75% H-phase at the beginning of the pressure ramp up. The phase fractions remain fairly constant up to 325 bar, where the D-phase converts to H-phase. The sample remains all H-phase after ramping pressure down to 50 bar. The phase transition for the **d100** sample at 291 K will be above 400 bar, the maximum pressure attainable.

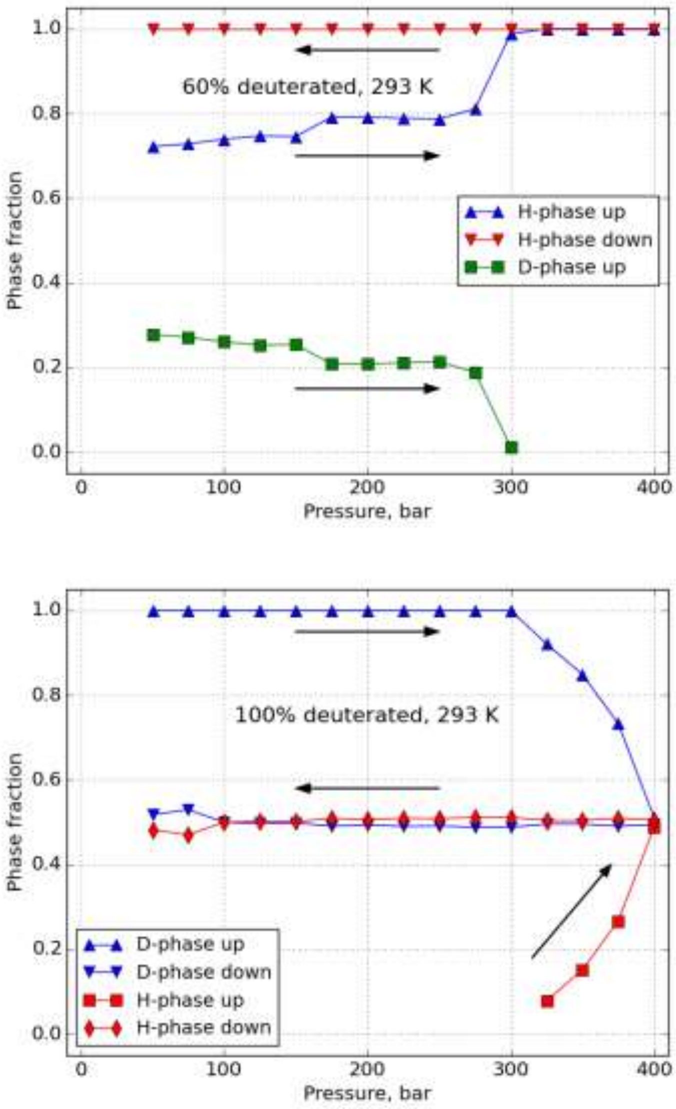

Figure S2 Phase fractions for 100% deuterated sample (**d100**) at 293 K. The sample is initially 100% D-phase at 50 bar. It begins transforming to H-phase at 300 bar. By 400 bar, the maximum pressure that was available, the sample is virtually 50/50 H-phase/D-phase. This does not change upon reducing pressure back to 50 bar. It is surmised that higher pressure would have transformed the entire sample to H-phase.

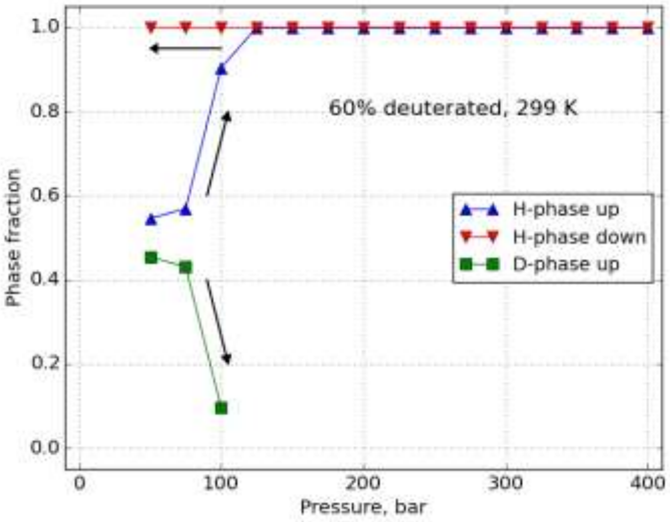

Figure S3 Phase fractions for 60% deuterated sample (**d60**) at 299 K. This sample is about 55% H-phase at the beginning of the pressure ramping up. It is converted to 100% H-phase by 125 bar. It remains 100% H-phase after ramping up to 400 bar and ramping down to 50 bar.

S2. Refinements against Single Crystal Neutron Diffraction Data from TOPAZ

Refinements were performed in GSAS (Larson & Von Dreele, 2004; Toby, 2001) using starting models, either H or D phase, from Simmons *et al*. (Simmons *et al.*, 1993). The initial H/D ratios were set to nominal H/D composition from the synthesis. The number of parameters was gradually increased until all the positional parameters and all anisotropic displacement parameters (ADPs) were refined.

The final refinement includes one occupancy variable for the H/D ratio in the ammonium ion and another H/D occupancy variable for the water molecules coordinating to Cu. The positions of the H/D atoms are constrained to be identical. Furthermore the ADPs for H and D atoms have been constrained such that $U_{ij}(\mathrm{H}) = \sqrt{2}U_{ij}(\mathrm{D})$ (Henning *et al.*, 2000). The models were refined against all data until converged. After convergence the outliers were removed based on the following criteria:

$$\frac{F_{obs}^2}{F_{calc}^2} > 5$$

$$\frac{F_{calc}^2}{F_{obs}^2} > 5$$

$$\frac{\left|F_{obs}^2 - F_{calc}^2\right|}{\sigma(F_{obs}^2)} > 5$$

Finally the models were refined against the remaining data.

S2.1. Temperature dependence of 60.3% D (d60) phase

Full datasets were collected on the same **d60** crystal at 100 K, 150 K, 200 K, 250 K and 295 K. The lattice constants of **d60** show changes consistent with those reported for the fully deuterated structure (Hathaway & Hewat, 1984) [Hathaway, B. J. & Hewat, A. W. (1984). *J. Solid State Chem*. **51**, 364-375]. The temperature dependence of the unit cell parameters are shown in Figure S4.

We measuared two **d60** crystals. The first one was used for the temperature series, i.e. was cooled to 100 K and subsequently heated in 50 K steps. To make sure it didn't loose deuterium or change otherwise, we measured a fresh crystal afterwards to be able to compare the two datasets. The thing we learned was that the refined D/H ratio changes a little as a function of temperature, but the D/H ratio does not change while the crystal in the nitrogen stream.

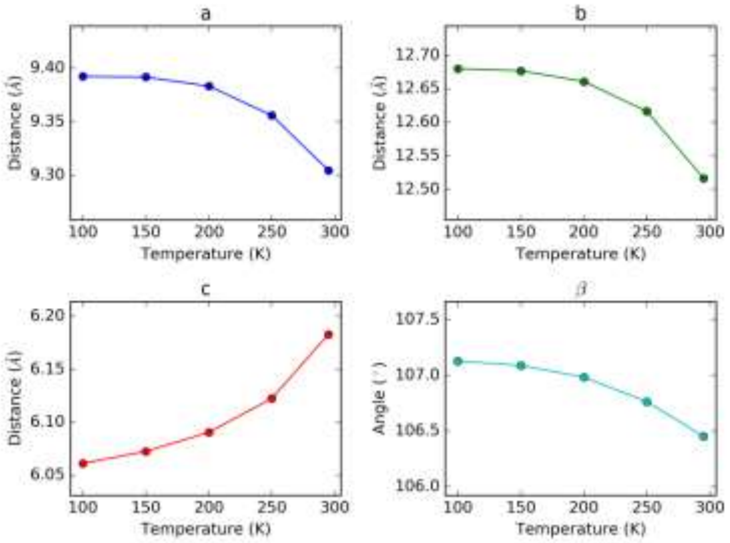

Figure S4 Unit cell parameters for the **d60** sample as a function of temperature. Error bars are smaller than the markers.

Selected bond lengths as function of temperature are plotted in Figures S5-S8. Figure S5 depicts the bond lengths around the Jahn-Teller distorted Cu(1) site. At low temperature it is clear that the Cu(1)-O(8) is elongated, which is a trait of the D-phase. Above 200 K the Cu(1)-O(8) bond starts to shorten along with an increase in the Cu(1)-O(7) bond. The Cu(1)-O(9) bond length is nearly constant. These trends are consistent with the fully deuterated compound (Hitchman *et al*., 1999) .

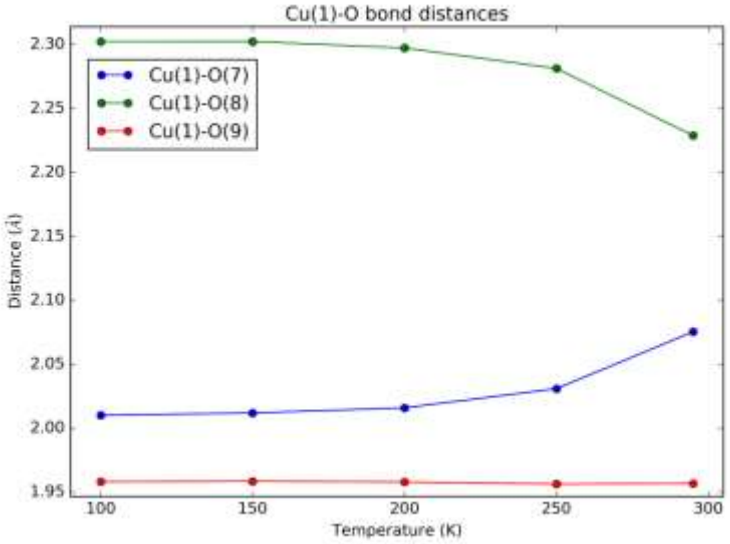

Figure S5 Bond lengths between Cu(1) and O in the **d60** sample as a function of temperature. Error bars are smaller than the markers.

All sulfur-oxygen bonds and nitrogen-hydrogen/deuterium bonds decrease in lengths with increasing temperature. This could indicate undescribed anharmonic motion or libration of the ions. Anharmonic motion for the H/D atoms on the ammonium ion was introduced in the models using the Gram-Charlier expansion (Johnson & Levy, 1974) [Johnson, C. K. & Levy, H. A. (1974). International Tables for X-ray Crystallography, Vol. IV. Burmingham, England, Kynoch Press.]. The introduction of the additional parameters, 25 per atom – 100 in total, did only improve the refinements slightly and only a few of the parameters refined to values lager than 3 σ. This is especially the case for the higher temperatures, where the number of significant data points is reduced due to thermal motion and thus the confidence in the advance model is lower. Therefore, we continue with the harmonic model, despite its apparent shortcomings.

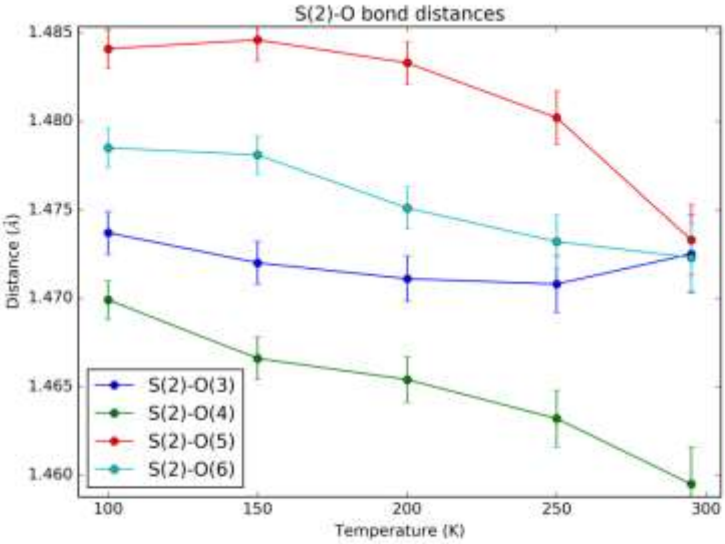

Figure S6 Bond lengths between S(2) and O in the **d60** sample as a function of temperature.

Of the sulfur-oxygen bonds, the S(2)-O(3) bond behaves anomalous and increases slightly in length between 250 K and 295 K. As shown in figure S2, the crystal is in the D-phase at low temperature and at higher temperature a higher and is excited to the H-phase this means a shift from ‘pure’ D(13)-O(4) hydrogen bonding to a mix of D(13)-O(4) and D(13)-O(3) bonding. This can also be seen in the bond length, figure S4, where the D(13)-O(4) bond length is increasing as a function of temperature and the D(13)-O(3) is decreasing. The N(10)-D(13) does not appear to show any different behaviour compared to the other N(10)-D bonds.

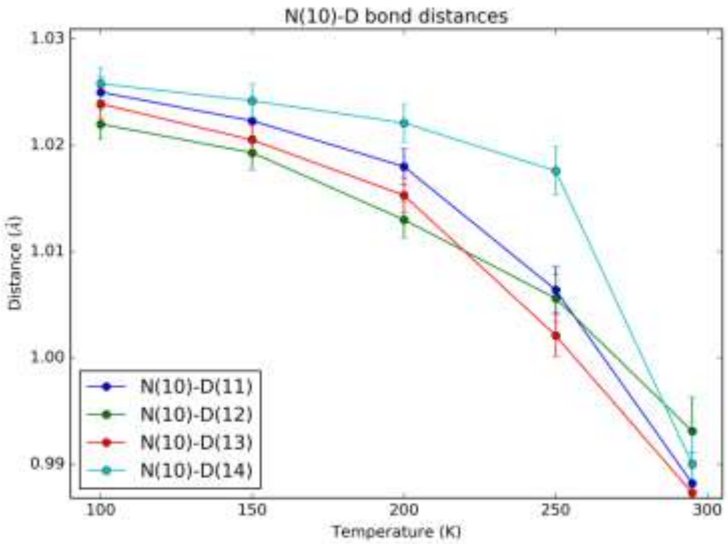

Figure S7 Bond lengths between N(10) and D atoms in the **d60** sample as a function of temperature.

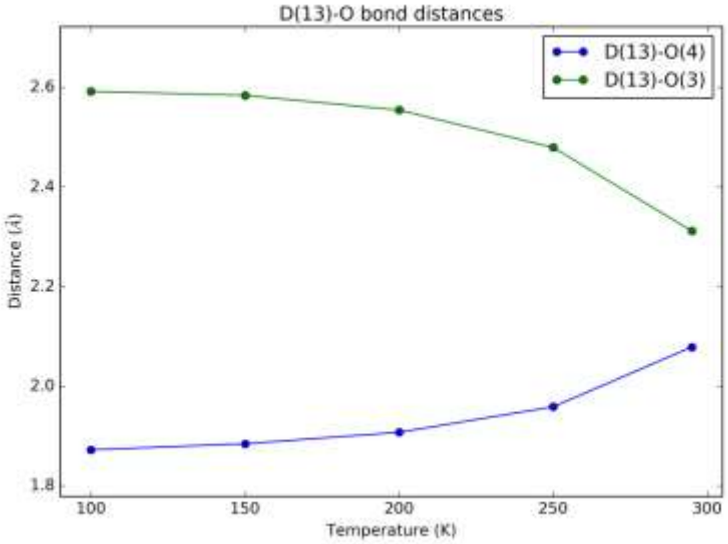

Figure S8 Bond lengths between D(13) and O in the **d60** sample as a function of temperature. Error bars are smaller than the markers.

The ADPs of D/H atoms on the ammonium ion is highly anisotropic consistent with liberation as mentioned above. The equivalent isotropic ADPs ($1/3\sum_{i=1}^{3} U_{ii}$) are shown in Figure S9. It is clear that the thermal parameters of the ammonium hydrogen (circles in figure S6) increase more than the hydrogen on the water molecules. Additionally it is also seen that the ADP of D(13) which in involved in the hydrogen bonds is increasing more than the others. A similar trend is seen for O(3) and O(4) where the ADPs increase more than for O(5) to O(8).

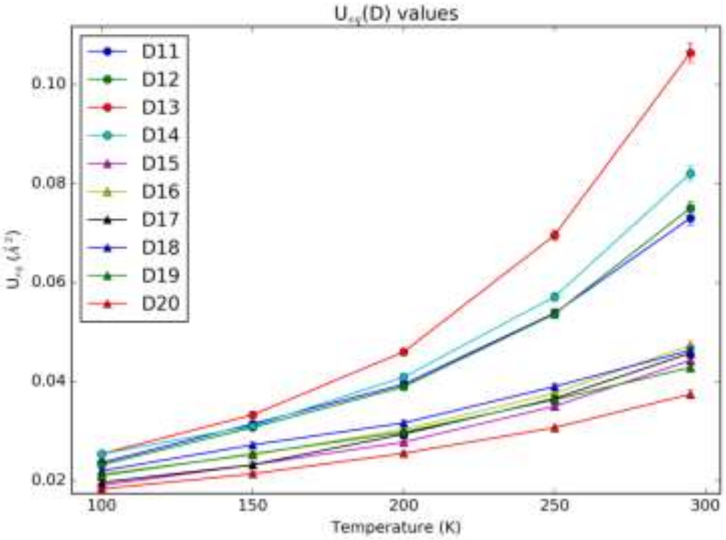

Figure S9 Equivalent ADPs , U_{eq}, for the deuterium atoms in **d60** sample as a function of temperature. Deuterium in NH_4^+ is marked with circles and deuterium in H_2O is marked with triangles.