

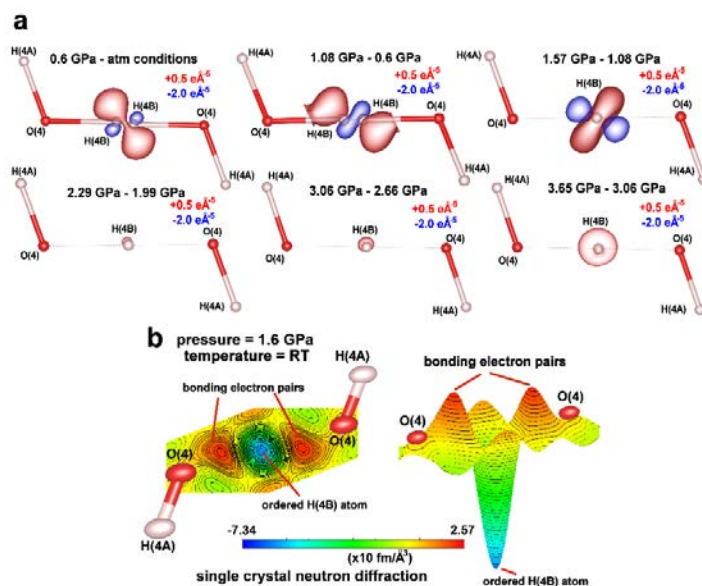
# Symmetrization of strong hydrogen bond under high pressure in bihydroxide-ion-containing $\text{NaCu}_2(\text{SO}_4)_2 \cdot \text{H}_3\text{O}_2$ revealed by experimental charge density and single crystal electron and neutron diffraction study

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The hydrogen bond symmetrization leads to a change in bulk modulus,<sup>1</sup> seismic wave velocities,<sup>1</sup> proton mobility and plays a primary role in the high temperature superconductivity,<sup>2</sup> but its characteristics are not well understood due to lack of systematic studies and limitations of experimental methods sensitive to this subtle change. In this work we present the most detailed study of pressure-induced hydrogen bond symmetrization process reported so far, utilizing for the first time single crystal electron and neutron diffraction methods to investigate this phenomenon along with experimental charge density analysis based on synchrotron X-ray diffraction data. On the way to the symmetrical H-bonding, natrochalcite mineral undergoes a series of complex redistributions of electron density which we traced with multipole refinement and detailed analysis of changes in the Laplacian of electron density values (Fig. 1a). The neutron diffraction experiment clearly indicated that hydrogen bond symmetrization takes place at  $\sim 1.6$  GPa and it is in the perfect agreement with the results from multipole refinement against X-ray data. Two symmetrically dependent maxima peaks between oxygen atoms and ordered H-atom visible on both maps (Fig 1b) are associated with localization of bonding electron pairs between the O(4) and H(4B) atoms. It shows that symmetric H-bond under high pressure conditions has unusually strong covalent character and its formation can have significant influence on physical properties of mineral structures under conditions in the Earth's mantle.



**Figure 1.** (a) 3D maps of differences in negative Laplacian values for the H(4B) atom. (b) Difference Fourier maps calculated using the model without hydrogen atom H(4B) refined against neutron data at 1.6 GPa.

- (1) Sano-Furukawa, A.; *et al.*, *Scientific Reports* 2018 8:1 2018, 8 (1), 1–9. <https://doi.org/10.1038/s41598-018-33598-2>.
- (2) Errea, I.; *et al.*, *Nature* 2016 532:7597 2016, 532 (7597), 81–84. <https://doi.org/10.1038/nature17175>.