# Symmetrization of strong hydrogen bond under high pressure in bihydroxide-ion-containing NaCu2(SO4)2∙H3O2 revealed by experimental charge density and single crystal electron and neutron diffraction study

## Piotr Rejnhardt1, Roman Gajda1, Magdalena Woińska1, Jan Parafiniuk2, Gerald Giester3, Ronald Miletich3, Yan Wu4, Tomasz Poręba5, Mohamed Mezouar5, Szymon Sutuła6, Tomasz Góral6, Przemysław Dera7, Krzysztof Woźniak1

### 1Department of Chemistry, University of Warsaw, Pasteura 1, Warszawa, 02-089, Poland.

### 2Department of Geochemistry, Faculty of Geology, University of Warsaw, Żwirki i Wigury 93, 02-089, Warszawa, Poland.

### 3Department of Mineralogy and Crystallography, University of Vienna, Josef-Holaubek-Platz 2, Vienna A-1090, Austria.4Neutron Scattering Division, Oak Ridge National Laboratory, Oak Ridge, Tennessee 37831, USA.5ID27 High Pressure Beamline, European Synchrotron Radiation Facility (ESRF), 71 avenue des Martyrs, 38000 Grenoble, France. 6Centre of New Technologies, University of Warsaw, S. Banacha 2c, 02-097, Warsaw, Poland

### 7Hawai'i Institute of Geophysics and Planetology, University of Hawai’i at Manoa, 1680 East-West Road, Honolulu, HI 96822, USA.

### p.rejnhardt@uw.edu.pl

The hydrogen bond symmetrization leads to a change in bulk modulus,1 seismic wave velocities,1 proton mobility and plays a primary role in the high temperature superconductivity,2 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 ~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.

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 (2) Errea, I.; *et al.*, *Nature 2016 532:7597* 2016, *532* (7597), 81–84. https://doi.org/10.1038/nature17175.