



IFMP Seminar

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Speaker **Piotr Rejnhardt**
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Title **Tracing the Mechanism of Hydrogen-Bond Symmetrization in Natrochalcite Under High Pressure by Experimental Charge Density Redistributions**

Abstract Natrochalcite is a rare mineral, found only in Chile, France, Greece, the USA, and Italy [1]. It crystallizes in the monoclinic space group $C2/m$, is usually emerald green in color, and has gained importance in recent years as an anode material for lithium-ion batteries [2]. Natrochalcite-type compounds have very rare $H_3O_2^-$ units with the shortest low-barrier hydrogen bond (HB) reported so far in hydrogen-bearing solids ($O\cdots O$ distance = 2.445 Å)[3]. Previous single-crystal neutron-diffraction experiments showed that hydrogen between two oxygen atoms is split into two positions with half occupancy at atmospheric conditions [4]. To the best of our knowledge there are only a few experimental works about the behavior of strong hydrogen bonds at high pressure, all on powder samples. We present for the first time the mechanism of HB symmetrization which leads to a new phase of natrochalcite using distributions of experimental electron density obtain by multipole refinement of very high resolution ($d = 0.32$ Å) single-crystal X-ray diffraction data at different pressures.

HB symmetrization in natrochalcite occurs between 1.08 and 1.57 GPa and shows that the low-barrier \rightarrow single-well HB transition is first-order. The symmetrization starts when the donor-acceptor distance $O(4)\cdots O(4)$ is $\sim 2.440(1)$ Å. This is in excellent agreement with previous *in-situ* 1H -NMR work [5], where an average critical $O\cdots O$ distance for maximum hydrogen mobility occurred at 2.443(1) Å. Our results show that HB symmetrization leads to a large decrease in $O\cdots O$ distance. Calculated 3D maps of the Laplacian of the experimental electron density show that this is accompanied at 1.08 GPa by a significant deformation of the valence electron density of the $O(4)$ atom participating in the HB symmetrization and the appearance of a depletion region for the disordered hydrogen atoms. This leads to an attractive interaction, which assists the proton transfer through the short H-bond and the of tunneling of protons increases just before the symmetrization. The topological analysis of the bond critical points (BCP) for the short H-bond reveal that after symmetrization, the Laplacian of the electron density at the BCP has a negative value, indicating that the symmetric H-bond has covalent character. At higher pressures, bonding densities get closer to the hydrogen atom and at 3.65 GPa we observe charge transfer across the symmetric hydrogen bond.

- [1] Powder pattern, natural sample from Chuquicamata, Chile. ICDD 19-1189. 2.797 (10). 6, (2001).
[2] Z. Liu *et al.*, *Evaluation of Low-cost Natrochalcite $Na[Cu_2(OH)(H_2O)(SO_4)_2]$ as an Anode Material for Li- and Na-ion Batteries*, *Electrochim. Acta* **211**, 619–626 (2016).
[3] R. Krickl *et al.*, *Crystal chemistry of synthetic Co- and Ni-analogues of natrochalcite — the shortest known hydrogen bonds among mineral-type compounds Part I: Single-crystal X-ray structures*, *Eur. J. Mineral.* **19**, 805–816 (2007).
[4] G. Chevrier *et al.*, *Neutron refinements of $NaCu_2(H_2O)_2(SO_4)_2$ and $RbCu_2(H_2O)_2(SeO_4)_2$: Variation of the hydrogen bond system in the natrochalcite-type series*, *Z. Krist.* **206**, 7–14 (1993).
[5] T. Meier *et al.*, *Structural independence of hydrogen-bond symmetrisation dynamics at extreme pressure conditions*, *Nat. Commun.* **13**, 3042 (2022).

Host: D. Peets