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Disorder of the $(\text{NH}_4)_3\text{H}(\text{SO}_4)_2$ in the high-temperature phase I : single crystal neutron diffraction. Yoo Jung Sohn^a, Karine Sparta^a, Sebastian Prinz^a, Martin Meven^b, Helmut Klapper^a, Georg Roth^a, Gernot Heger^a, ^a*Institut für Kristallographie, RWTH Aachen University, Germany*, ^b*ZWE FRM-II, TU München, Germany*
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Triammonium hydrogen disulfate $(\text{NH}_4)_3\text{H}(\text{SO}_4)_2$ (TAHS) has gained a continuous interest over a few decades. One of the reasons is the great number of structural phase transitions [1] and the other aspect is the superprotonic conductivity in the high-temperature phase I [2,3]. Single crystals of TAHS were grown from aqueous solution by slow evaporation. A sample of $3 \times 3 \times 3 \text{ mm}^3$ was used for the single crystal neutron diffraction experiments. By heating up the sample we observed the II-I phase transition from monoclinic to rhombohedral and the high-temperature measurements were carried out at 413(2) K. A complete dataset of Bragg reflection intensities was collected up to $(\sin\theta/\lambda)_{\text{max}} = 0.9 \text{ \AA}^{-1}$ on the four-circle diffractometer HEiDi at the FRM II in Garching with a wavelength of $\lambda = 0.555 \text{ \AA}$ (Cu(420) monochromator). The crystal structure of TAHS-I was refined using JANA2006 [4]. The characteristic feature of the structure of TAHS in the monoclinic room-temperature phase is the strong hydrogen bonding between two SO_4 -tetrahedra forming isolated $(\text{SO}_4)\text{H}(\text{SO}_4)$ -dimers. The hydrogen atom in the middle of the $(\text{SO}_4)\text{H}(\text{SO}_4)$ -dimer is dynamically disordered according to the central inversion symmetry -1 . Using a split-atom model the O1-H1 and O1-O1 distances are 0.99(1) Å and 2.549(7) Å, respectively [5]. The crystal structure of TAHS-I is rhombohedral, space group R-3m with lattice parameters $a = 5.907(3) \text{ \AA}$, $c = 22.57(1) \text{ \AA}$. One of the distinctive features of TAHS-I is the disorder of the O-atom building the top of the SO_4 -tetrahedron [6]. Instead of lying on a three fold axis, it takes a more general position and is splitted in three equivalent positions. Each of these splitted O-atoms is involved in the hydrogen bond and together they build a hydrogen bond network, which allows a pathway for the superprotonic conductivity [7]. Corresponding to the model in the room-temperature phase we also treated the hydrogen atom involved in the hydrogen bond with a split-atom model. As a result we found an O1-H1 distance of 0.94(2) Å and an O1-O1 distance of 2.650(5) Å. A possible contribution of the NH_4 -groups to the superprotonic conductivity was also supposed with the crystal structure analysis.

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