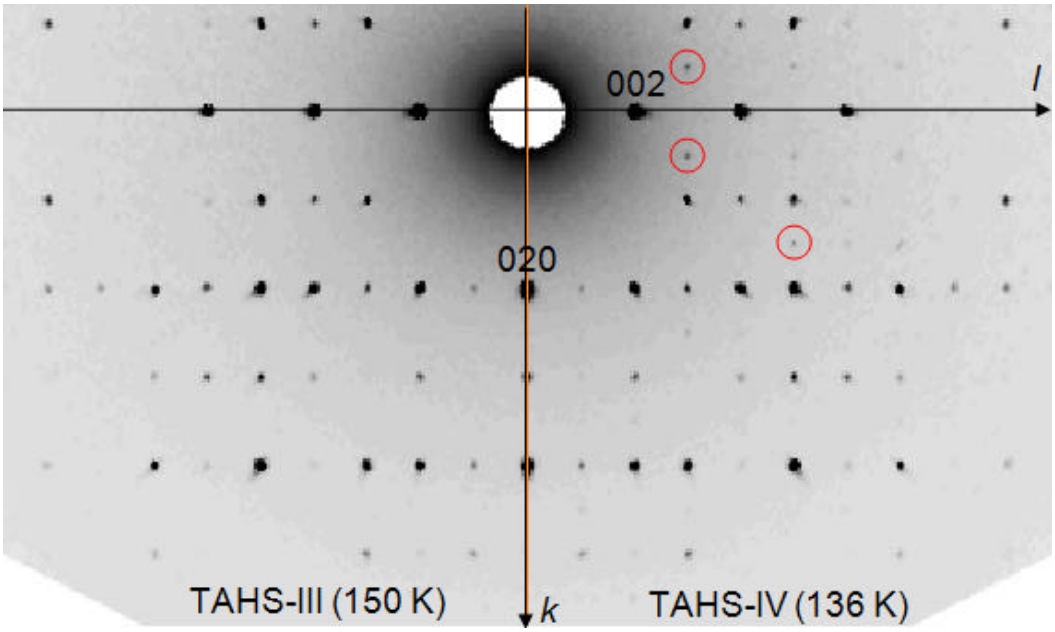
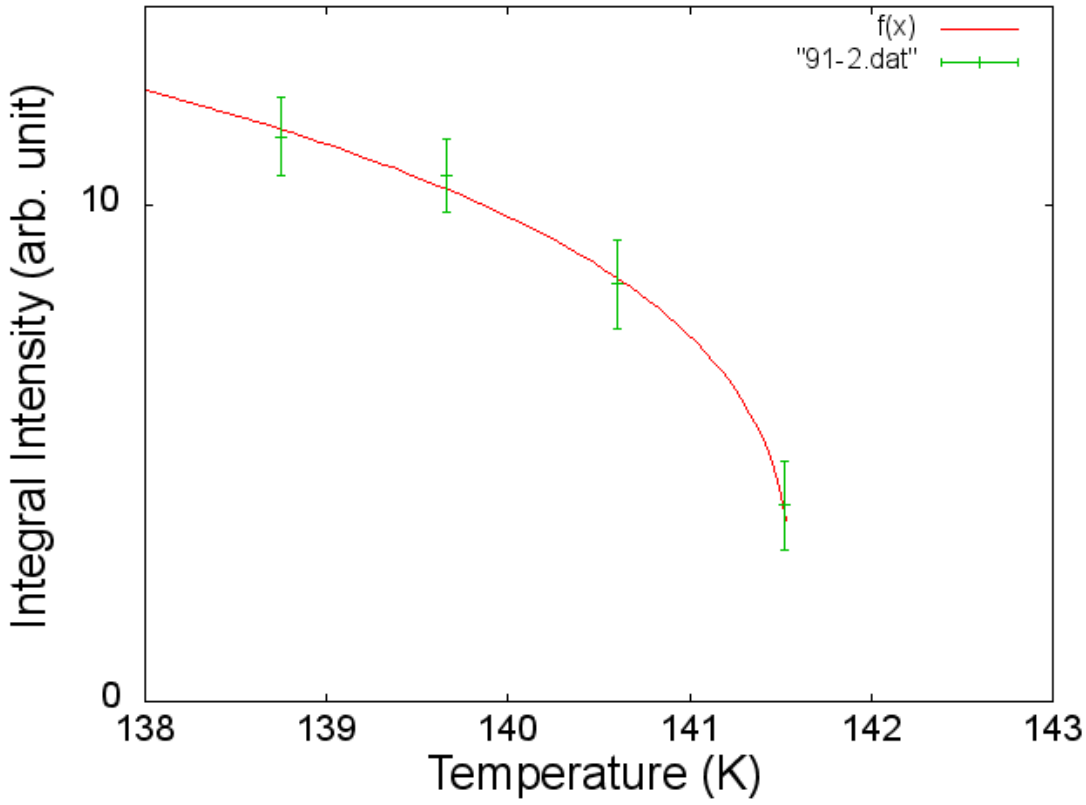
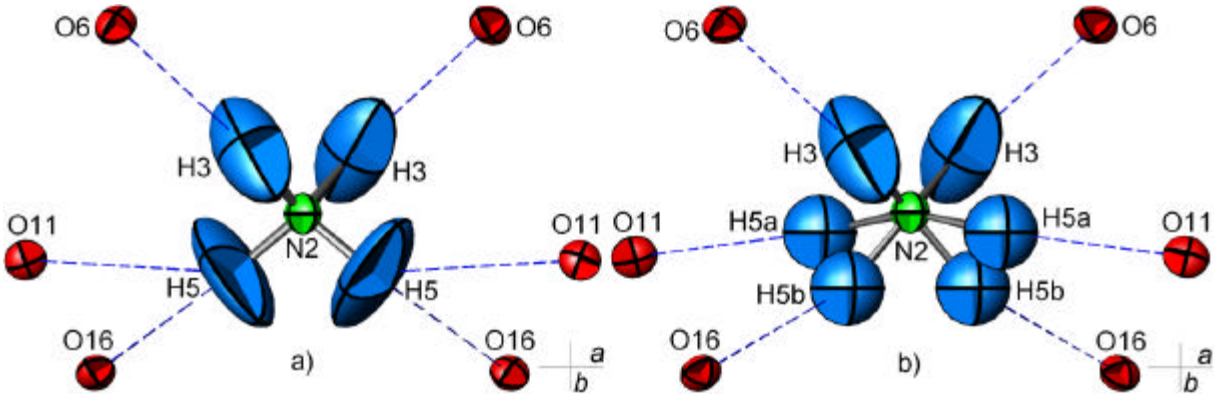


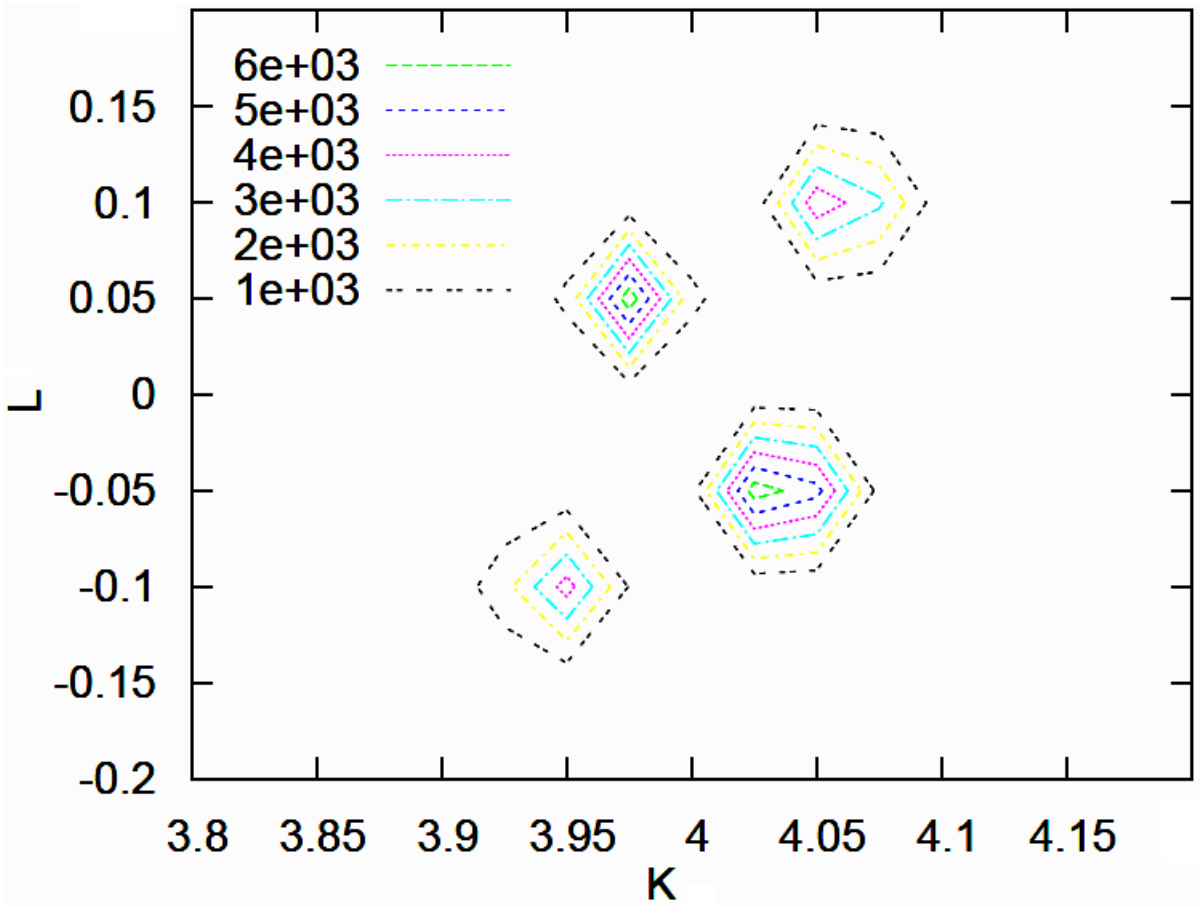
S01: Additional interlayer reflections (marked with a circle) at 136 K using an image-plate diffractometer (STOE-IPDS II) in the *(0kl)* plane, indicating a doubling of the unit cell in **b** direction in TAHS-IV.



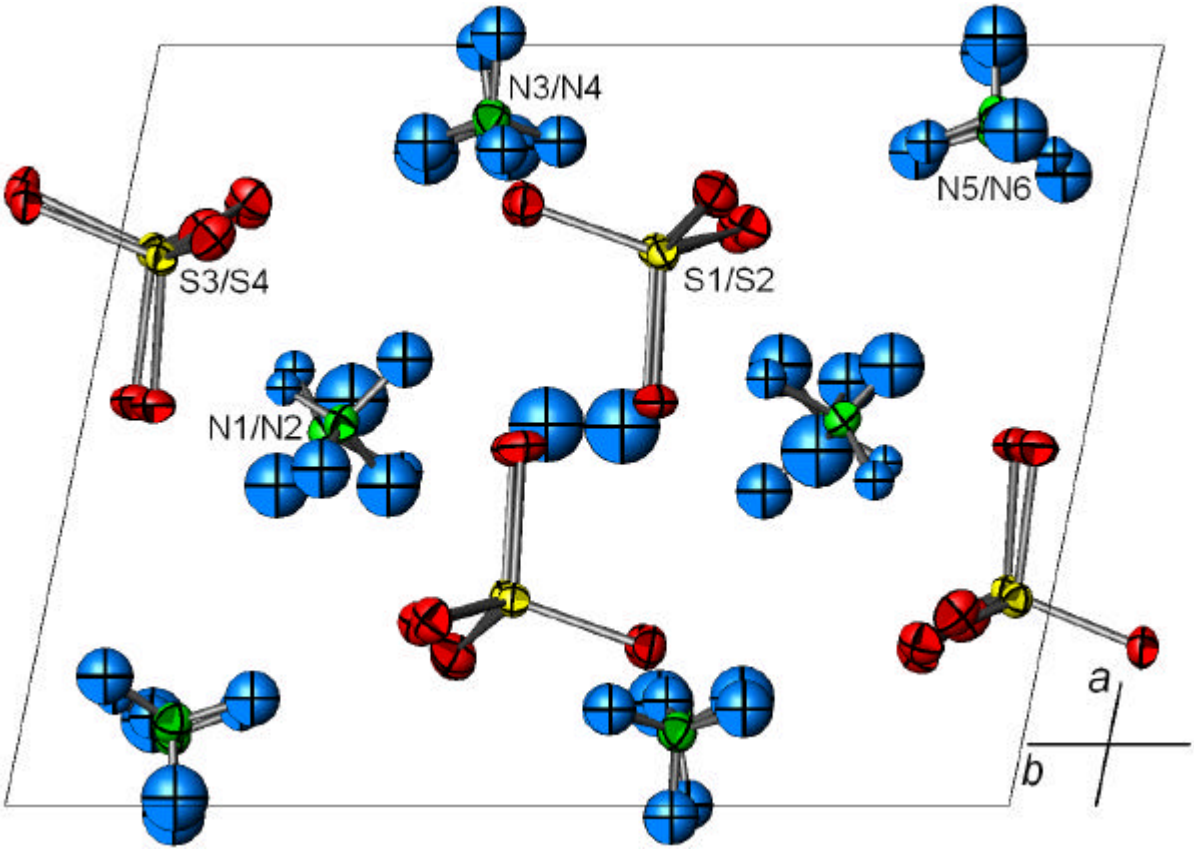
S02: Integral intensity of the superstructure reflection 91-2 by single-crystal neutron diffraction in TAHS-IV on heating as a function of temperature.



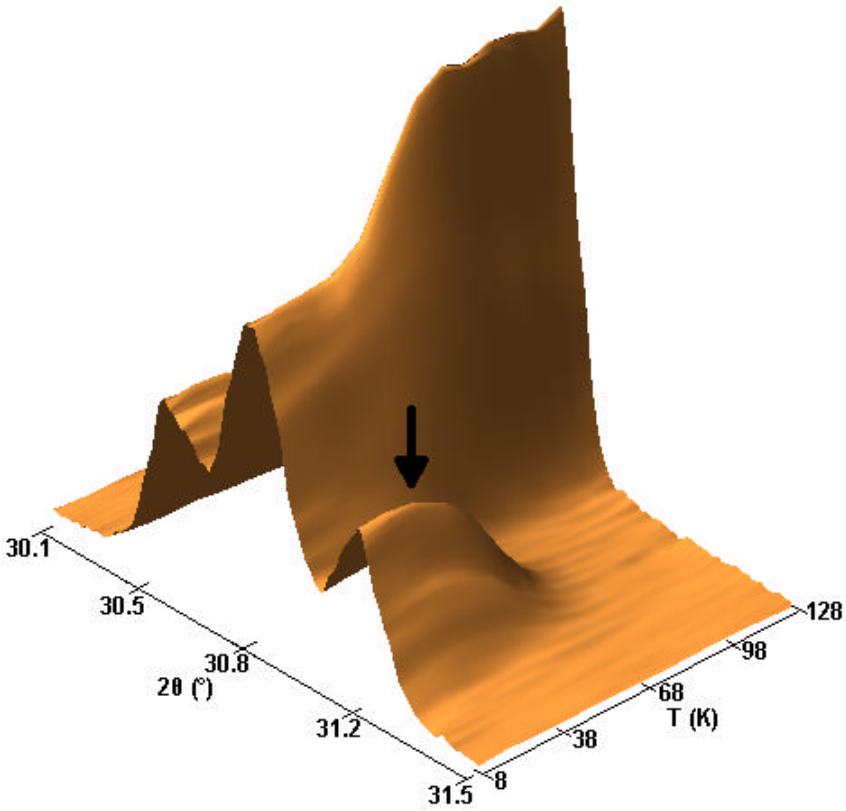
S03: NH_4^+ group on a special position with its surrounding O atoms in TAHS-IV. a) Non-split and b) split model. Displacement ellipsoids are drawn at the 50 % probability level.



S04: Q-Scan measurements of the reciprocal *(0kl)* plane.



S05: Unit cell of triclinic TAHS-V (P-1) at 126 K by single-crystal X-ray diffraction studies. Displacement ellipsoids are drawn at the 50 % probability level.



S06: Additional peak of TAHS-VII in the X-ray powder pattern on cooling.