X-ray diffraction and NMR spectroscopy of $Rb_3D_xH_{1-x}(SO_4)_2$

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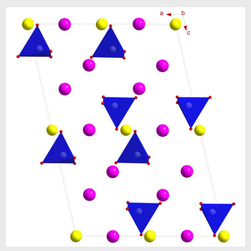
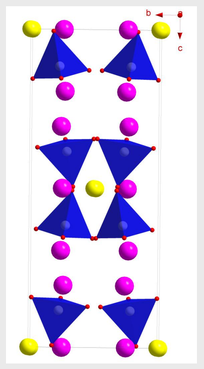
Experimental

- The compounds $Rb_3D(SO_4)_2$ and $Rb_3H(SO_4)_2$ are members of the $M_3H(XO_4)_2$ family where the H-bonds play an important role for the understanding of aqueous systems. Protonated and deuterated single crystals were grown from aqueous solution by courtesy of A. Maiazza (TU Darmstadt).
- A four circle HUBER diffractometer with a closed cycle He-cryostat (CTI-Cryogenics) in front of a SCHNEIDER rotation anode and an OSMIC multilayer monochromator for Cu Kα radiation were used for the X-ray experiments.
- X-ray studies on single crystals of were performed as a function of temperature between 10 K and 300 K.
- Determination of the lattice parameters as a function of temperature using 60 reflections with a high 2ϑ-value at both sides of the primary beam (STOE STAD4 program system).
- The NMR measurements were carried out using the quadrupole perturbed central transition (1/2 $\rightarrow$ -1/2) of the ^{87}Rb (I = 3/2) nucleus; the Larmor frequency was ν_L = 85.7 MHz.

The basic structure of $Rb_3H(SO_4)_2$

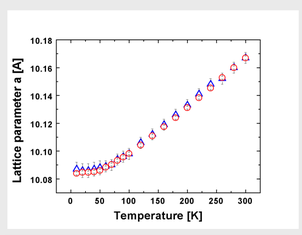


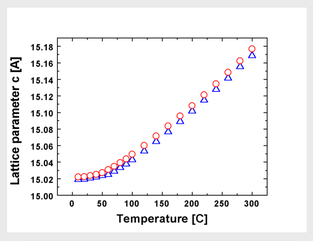
SO_4 Rb H

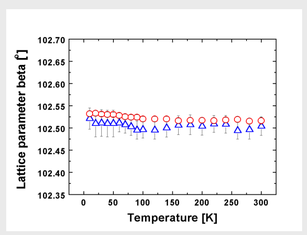


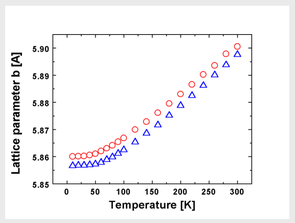
SG = A2/a, Z=4,
a_0=10.47 Å, b_0=6.09 Å, c_0=15.42 Å, ß=102.9

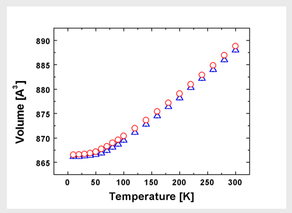
Variation of the lattice parameters of $Rb_3D(SO_4)_2$ and $Rb_3H(SO_4)_2$





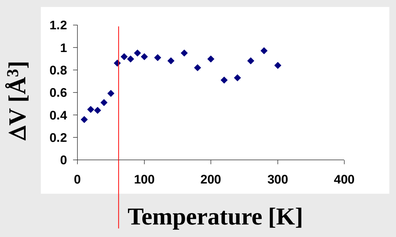


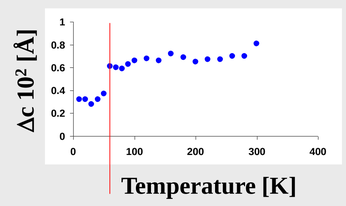




$Rb_3D(SO_4)_2$
$Rb_3H(SO_4)_2$

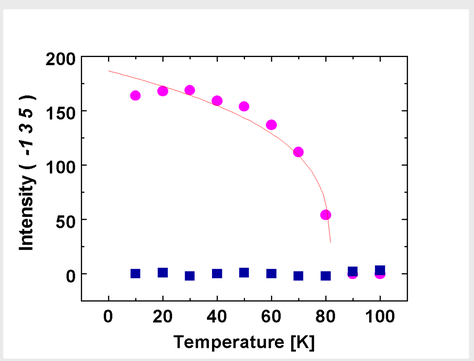
Difference between lattice parameters





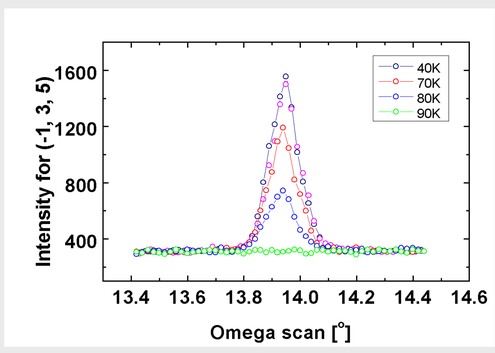
The difference between the lattice parameters of $Rb_3D(SO_4)_2$ and $Rb_3H(SO_4)_2$ exhibits a phase transititon at ≈ 80 K.

The paraelectric ⇔ antiferroelectric phase transition of $Rb_3D(SO_4)_2$



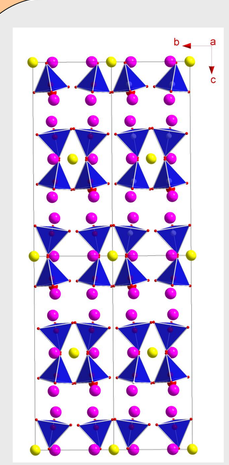
Intensity of *-1 3 5* of $Rb_3D(SO_4)_2$ ● and of $Rb_3H(SO_4)_2$ ■

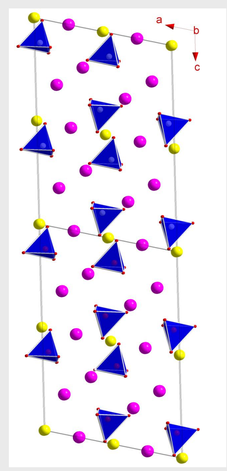
Fit: $I = a (T_N - T)^{2ß}$ T_N = 80.2 K ß = 0.109(1)

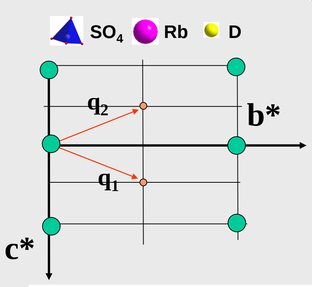


Omega scan of *-1 3 5* of $Rb_3D(SO_4)_2$ at various temperatures

The low temperature structure of $Rb_3D(SO_4)_2$



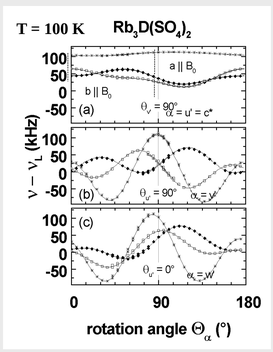




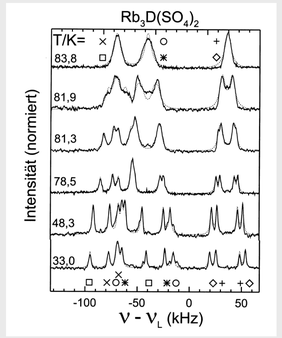
Diffraction diagram with main ● and superstructure ● reflections

SG = A2, Z=16,
a_0=10.47 Å, b_0=12.18 Å,
c_0=30.84 Å, ß=102.9

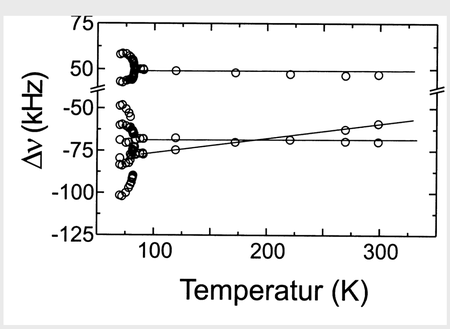
NMR spectroscopy



Resonance positions obtained by rotating about 3 mutually perpendicular axes for T > T_N



Spectra of $Rb_3D(SO_4)_2$. At T = T_N the number of resonance lines quadruples.



Line shifts as a function of temperature

Conclusion

- Studies reveal a paraelectric ⇔ to antiferroelectric phase transition at ≈ 80 K. The phase transition occurs in $Rb_3D(SO_4)_2$ but not in $Rb_3H(SO_4)_2$
- For $Rb_3D(SO_4)_2$: superstructure reflections appear in the antiferroelectric phase with two wave vectors $\mathbf{q}_1$= (0, ½, ½) and $\mathbf{q}_2$= (0, ½, –½). The low temperature structure must be described in a cell (*a, 2b, 2c*)
- The space group in the paraelectric phase is A2/a; for the antiferroelectric phase of $Rb_3D(SO_4)_2$ the space group A2 must be assumed.
- An analysis of rotation patterns recorded at 100 K and 78 K reveals small deviations from monoclinic symmetry. This loss of symmetry can be ascribed to the hydrogen-bond system.