

NEUTRON DIFFRACTION STUDY OF  
THE LOW-TEMPERATURE PHASE TRANSITION OF MN-LEONITE

by

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Single-crystal Time-Of-Flight (TOF) neutron diffraction data of Mn-leonite,  $K_2Mn(SO_4)_2 \cdot 4H_2O$ , were obtained at the Intense Pulsed Neutron Source (IPNS) at Argonne National Laboratory, Illinois, using a four-circle single-crystal diffractometer and a position-sensitive detector. Two reversible phase transitions at low temperatures have been previously confirmed by optical, calorimetric [1], and X-ray data [2]. The cause for the phase transitions of Mn-leonite is a dynamic disorder of sulphate groups  $S_dO_4$  at room temperature (C2/m), that freeze to an ordered structure (I2/a) at 205(1) K. At 169(1) K the crystal structure switches to another ordered phase (P2<sub>1</sub>/a).

At room temperature the structure of Mn-leonite consists of two crystallographically different  $MnO_6$  octahedra, assembled in the form of  $Mn[(H_2O)_4(SO_4)_2]_2$ - units, with the sulphate groups in trans conformation and the S–Mn–S axes oriented nearly parallel to [100]. They form layers parallel to (001), with each layer consisting solely of  $S_o$ – $Mn_1$ – $S_o$  (ordered layer) or  $S_d$ – $Mn_2$ – $S_d$  (disordered layer) units, respectively. The units are interconnected by potassium cations in [9]- or [10]- coordination and by hydrogen bonds of the  $H_2O$  molecules.

Because X-ray methods locate electron densities rather than nuclei of atoms, the obtained H coordinates represent the delocalized H electrons. In the case of Mn-leonite with a dynamic disorder in the room temperature crystal structure an additional influence of proton dynamics is probable. Hence, neutron diffraction is an excellent method to investigate the hydrogen bonds, which influence the cooperative arrangement of tetrahedra across the layers.

The crystal for the data collection was a clear, synthetic specimen, that was ground to an ellipsoid with a size of 2.5 x 2 x 2 mm, elongated parallel to a. The neutron diffraction data were collected at room temperature, in the interval between the two indicated transition temperatures at 185 K, and below the second transition at 110 K. Least-squares refinements of the neutron diffraction data were carried out using the program system PC-GSAS [3]. Lattice parameters and starting values for the atomic positional parameters were obtained from the X-ray refinements [2] at the corresponding temperatures.

The results at room temperature are in good agreement with the neutron diffraction refinement of SRIKANTA et al. [4] with a deviation of the atom coordinates of less than 1 %. The refined atomic positional parameters confirm the X-ray diffraction data, obtained at identical temperatures. With the neutron diffraction data the coordinates of the hydrogen nuclei are determined, by which the evolution of the hydrogen bonds during the transformation process is elucidated.

Comparison of the O–H...O angles confirms the rule, that stronger hydrogen bonds are straighter than weaker ones. Within the ordered layer the distortion of the structure with decreasing temperature is accompanied by continuous decreasing and increasing, respectively, of the two O–H...O bond lengths surrounding the  $S_o$  tetrahedra. In general, the H...O distances surrounding the  $S_d$  tetrahedra (disordered at room temperature) are longer  $< 1.78 \text{ \AA} >$  than the H...O distances surrounding the  $S_o$  tetrahedra  $< 1.72 \text{ \AA} >$ .

The interatomic distances and angles of the  $H_2O$  molecules are close to those of free water molecules [5], i.e. O–H =  $0.98 \text{ \AA}$  and H–O–H =  $104.5^\circ$ . At room temperature the O–H distances show the most significant deviations from the ideal value with the two shortest distances of  $0.945(5) \text{ \AA}$  and  $0.955(5) \text{ \AA}$ , belonging to the  $Ow3$  molecule, connecting the disordered sulphate tetrahedra with the ordered layers via hydrogen bonds. Hence, the dynamics of the  $Ow3$  molecule leads to the apparently shortened O–H distances, and, in addition, to enlarged  $U_{ij}$  values. The  $Ow2$  molecule, connecting the ordered tetrahedra within the ordered layer, is straightened to H–O–H =  $110^\circ$  in all three crystal structures.

## References

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