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Proton dynamics in letovicite: Part II. Static ^{2}H NMR experiments and lineshape simulations

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Abstract

Synthetic deuterated letovicite $(ND_4)_3D(SO_4)_2$ has been investigated using static ^{2}H NMR spectroscopy acquired with a quadrupolar echo sequence. Subsequently, the experimental signals were fitted with theoretical quadrupolar lineshapes to extract the quadrupolar coupling parameters. Experiments were carried out in the temperature range of 102–425 K. Two different signals were distinguished due to ammonium and free acidic deuterons. The ammonium deuterons show only small quadrupolar interaction at room temperature, which can be described best by a fast anisotropic dynamic reorientation of the tetrahedra leading to residual quadrupolar interaction. The dynamically averaged "static" quadrupolar coupling constant is C_Q = 2.4 kHz at room temperature. The development of C_Q as a function of temperature clearly indicates three phase transitions at 160, 260, and 400 K (triclinic $P1$ → monoclinic $P2/n$ or Pn → monoclinic $C2/c$ → rhombohedral $R\bar{3}m$). The asymmetry parameter η shows a similar behavior. It indicates strongest the monoclinic → monoclinic phase transition at 260 K. The lineshape corresponding to the free acidic protons is difficult to simulate because it is strongly superimposed by the dominant ammonium proton resonance. However, the decrease of the quadrupolar coupling constant of the signal from C_Q = 108 kHz at 130 K to 31.5 kHz above 370 K can be assigned to a time-averaging of the quadrupolar interaction due to the increased motion of the sulfate tetrahedra about their threefold axis, so that C_Q amounts to only 1/3 of the static quadrupolar coupling constant of the static spectrum at low temperatures.

Keywords: Letovicite, proton conduction, ferroelastic, ^{2}H, lineshape analysis, simulation, reorientation, solid state NMR, quadrupole echo