

## Proton dynamics in letovicite: Part I. Static $^1\text{H}$ and $^{15}\text{N}$ NMR MAS experiments and lineshape simulations

MICHAEL FECHTELKORD,<sup>1,\*</sup> ASTRID DIEKMANN,<sup>2</sup> AND ULRICH BISMAYER<sup>3</sup>

<sup>1</sup>Institut für Geologie, Mineralogie und Geophysik der Ruhr-Universität Bochum, Universitätsstrasse 150, 44780 Bochum, Germany

<sup>2</sup>Institut für Mineralogie der Universität Hannover, Welfengarten 1, 30167 Hannover, Germany

<sup>3</sup>Mineralogisch-Petrographisches Institut der Universität Hamburg, Grindelallee 48, 20146 Hamburg, Germany

### ABSTRACT

Synthetic letovicite  $(\text{NH}_4)_3\text{H}(\text{SO}_4)_2$  has been investigated using  $^1\text{H}$  static, low-speed MAS, and  $^{15}\text{N}$  MAS NMR spectroscopy. Experiments were carried out in the temperature range of 215–425 K. The  $^1\text{H}$  MAS NMR spectra show three different resonances. The resonance assigned to the ammonia protons is broad and spinning sidebands cannot be resolved in the low-speed MAS NMR spectra. On the other hand, the acidic protons in the ferro- and paraphase show narrow signals with sideband patterns that enable a chemical shift anisotropy analysis. The chemical shift parameters of the free protons in the paraphase ( $\delta_{\text{iso}} = 13.2$  ppm,  $\delta_{\text{aniso}} = 4.5$  ppm,  $\eta = 0.0$ ) differ completely from those of the protons in the ferrophase ( $\delta_{\text{iso}} = 14.1$  ppm,  $\delta_{\text{aniso}} = 8.5$  ppm,  $\eta = 1.0$ ). The lowering of the chemical shift anisotropy  $\delta_{\text{aniso}}$  by a factor of two and the change of the asymmetry parameter  $\eta$  imply a tetrahedral site jump mechanism of the protons. Three different ammonia tetrahedra can be distinguished by  $^{15}\text{N}$  MAS NMR spectroscopy in the  $P2/n$  phase below 273 K. Two resonances are prominent for the ferrophase (space group  $C2/c$ ) corresponding to the two different crystallographic sites. Both resonances move together into a single resonance in the high-temperature phase that can be interpreted as fast dynamics of ammonia groups and its local environment so that the two crystallographic sites are locally nearly equal.

**Keywords:** Letovicite, proton conduction, ferroelastic,  $^1\text{H}$ ,  $^{15}\text{N}$ , chemical shift anisotropy, lineshape analysis, reorientation, MAS, solid state NMR spectroscopy, phase transition