Proton dynamics in letovicite: Part I. Static ¹H and ¹⁵N NMR MAS experiments and lineshape simulations

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ABSTRACT

Synthetic letovicite $(NH_4)_3H(SO_4)_2$ has been investigated using ¹H static, low-speed MAS, and ¹⁵N MAS NMR spectroscopy. Experiments were carried out in the temperature range of 215–425 K. The ¹H 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 ($\delta_{iso} = 13.2 \text{ ppm}$, $\delta_{aniso} = 4.5 \text{ ppm}$, $\eta = 0.0$) differ completely from those of the protons in the ferrophase ($\delta_{iso} = 14.1 \text{ ppm}$, $\delta_{aniso} = 8.5 \text{ ppm}$, $\eta = 1.0$). The lowering of the chemical shift anisotropy δ_{aniso} by a factor of two and the change of the asymmetry parameter η imply a tetrahedral site jump mechanism of the protons. Three different ammonia tetrahedra can be distinguished by ¹⁵N 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, ¹H, ¹⁵N, chemical shift anisotropy, lineshape analysis, reorientation, MAS, solid state NMR spectroscopy, phase transition

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INTRODUCTION

Triammonium hydrogen disulfate (letovicite) belongs to the well-studied class of ferroelastic materials of general formula $M_3H(AO_4)_2$ (M = K, Rb, Cs, NH₄; A = S, Se). The name letovicite comes from the Czech village Lettowice where the mineral was first discovered in 1932. Natural deposits can be found in Bohemia (Czech Republic), Saxony (Germany), Hungary, and the United States. The monoclinic room-temperature phase is improper ferroelastic with space group C2/c and undergoes a phase transition at $T_c = 413$ K to a trigonal paraelastic high-temperature phase. The formation of domain boundaries first occurs at a temperature of 30 K below the phase transition temperature (Baranov et al. 1987; Merinov et al. 1990, 1991; Suzuki and Makita 1978). The structure (see Fechtelkord et al. 2000) can be described in space group $R\overline{3}m$ and consists of a double layer of sulfate tetrahedra with their bases parallel to the (001) plane. The tops of the tetrahedra of every other layer point toward each other. Furthermore, the tetrahedra of one layer are shifted with respect to those of the opposite layer along the (001) plane and form a corrugated network of six-membered rings. Acidic protons are located in SO-H…OS bonds in the center of these double layers connected to one sulfate tetrahedron of the upper layer and one of the lower layer. The ammonium tetrahedra are

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Previous investigations have shown that the mechanism of the phase transition is dominated by a combination of order/ disorder effects of the acidic protons as well as displacements and reorientations of the ammonium tetrahedra perpendicular to the threefold inversion axis along the three binary axes of the ferrophase (Schwalowsky et al. 1998). Separating the dynamic behavior of acidic protons and the ammonium groups by 1H MAS and static 14N NMR spectroscopy allowed the examination of local processes and coupling effects concerning the phase transition (Fechtelkord et al. 2000). The ¹H MAS NMR resonance from ammonium was distinguished from that of acidic protons. A third resonance appeared just below the phase transition temperature caused by the acidic protons in the paraelastic phase. The lowering of the second moment M_2 (which is the mean quadratic line width) for the ammonium protons took place in the same temperature range as the formation of domain boundaries, while

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located at two different crystallographic positions. On the one hand, they form double layers alternating with the sulfate double layers (N2 site). On the other hand they are located in the center of the six-membered rings of the sulfate double layers (N1 site). In comparison with the paraelastic phase, the ammonium and sulfate tetrahedra are tilted from their original orientations in the ferroelastic low-temperature phase. Furthermore, the ammonium tetrahedra are displaced perpendicular to the threefold inversion axis of the paraphase along the binary axes of the ferroelastic phase.

the signals of the acidic protons indicated a line narrowing in the area of T_c . The static ¹⁴N NMR spectra confirmed the critical temperature of the motional changes of the ammonium tetrahedra. Two-dimensional ¹H nuclear overhauser effect spectroscopy (NOESY) spectra indicated a chemical exchange between ammonium protons and the acidic protons of the paraphase.

Another characteristic property of letovicite is its superprotonic conductivity in the paraelastic phase. In the trigonal paraelastic phase the centers of the three SO-H-OS bonds are distributed over the 9e Wyckoff positions forming a dynamically disordered hydrogen bond network (DDHBN). This effect enables a superprotonic conductivity of $\sigma_a^{dc} = \sigma_b^{dc} = 10^{-2}$ S cm⁻¹ in the (001) plane (Baranov et al. 1989; Merinov 1996; Schwalowsky et al. 1998). Substantial conductivity exists also perpendicular to the (001) plane along the trigonal c-axis (σ_c^{dc} = 10⁻⁴ S cm⁻¹). The conductivity pathways of the protons along the c-direction were theoretically considered by Merinov (1996). The author assumed supplementary hydrogen bonds between sulfate groups of different double layers and relatively high protonic conductivity along the [001] direction. Moreover he determined that the ammonium groups located in the sulfate double layers participate in the proton conduction process in the (001) plane (Merinov et al. 2000).

The aim of the present study is to investigate the local dynamic processes of the acidic protons as well as those of the ammonia tetrahedra and their relation to the phase transition to obtain improved knowledge about the superprotonic conductivity and the formation of ferroelastic domains. This information can be achieved by one of the most important interactions in solid state NMR spectroscopy, the chemical shift interaction (CS). It is caused by the external field, which induces motion of the electrons such that a secondary magnetic field is set up. The secondary field produced by this current loop opposes the main field at the nucleus. Thus, the nucleus is either shielded (diamagnetic effect) or de-shielded (paramagnetic effect). The resulting field is lower or higher than the static magnetic field. This means the chemical shift interaction directly corresponds to the electron distribution in the electron shell, which depends on the local coordination of the measured nucleus (Fechtelkord 2004). Static and low-speed MAS ¹H and ¹⁵N MAS NMR spectroscopy in connection with subsequent lineshape simulation is an ideal technique to separate the contributions of acidic and ammonium protons due to their different chemical shifts. The chemical shift interaction is anisotropic and depends on the orientation of the local environment related to the outer static magnetic field. Alterations in the chemical shift anisotropy lineshape of the contributing ¹H resonance correlate strongly with changes in dynamic processes of the participating distinct hydrogen species.

The two different ammonium tetrahedral sites can be distinguished with ¹⁵N MAS NMR spectroscopy. Experiments were carried out at temperatures from 215–425 K, and it is shown that the dynamics of the ammonium as well as the sulfate tetrahedra increases such that the two crystallographically different ammonium sites become undistinguishable in the ¹⁵N MAS NMR spectra.

¹H and ¹⁵N NMR spectroscopy can only contribute information about the change of dynamics, but not about the type. In part II of this work (Fechtelkord et al. 2007), one of the most extensively used techniques, i.e., static solid-state ²H NMR spectroscopy, is used together with ²H NMR lineshape analysis to deal as a particularly sensitive probe of motional mechanism with characteristic time scales in the range 10⁻³–10⁻⁸ s (the so-called "intermediate motional range").

EXPERIMENTAL METHODS

Single crystals of $(NH_4)_3H(SO_4)_2$ and $(^{15}NH_4)_3H(SO_4)_2$ were grown in a temperature-controlled heating chamber by slow evaporation at \approx 314 K from an aqueous solution containing 40 wt% $(NH_4)_2SO_4$ or $(^{15}NH_4)_2SO_4$ (60% ^{15}N isotope-enriched, Sigma-Aldrich Chemie GmbH, München), 20 wt% H₂SO₄ or D₂SO₄ (Deutero GmbH, Kastellaun), and 40 wt% H₂O or D₂O (Deutero GmbH, Kastellaun) (Gesi 1976). D₂SO₄ and D₂O were used to reduce the heteronuclear dipolar interaction between ^{15}N and ¹H. The grade of deuteration of the partially deuterated ^{15}N -enriched samples was estimated to be 59 ± 7% by ¹H MAS NMR spectroscopy. Transparent colorless pseudo-hexagonal plates crystallized with a predominant (001) face. Subsequently the crystals were characterized by X-ray powder diffraction to check their phase purity.

¹H static and low-speed MAS NMR spectra were obtained at 400.13 MHz using a BRUKER ASX 400 NMR spectrometer with a 7 mm standard Bruker MAS probe. A HAHN solid echo $[90_x - \tau - 180_y - \tau - (acq)_x]$ was applied in the static experiment. The 90 and 180° pulse lengths were 6.0 and 11.7 µs, respectively. The delay was set to $\tau = 40$ µs. The spectra were accumulated using a spectral width of 125 kHz and a recycle delay of 10 s. Typical conditions for the ¹H low-speed MAS NMR spectra were pulse lengths of 4.0 µs (90° pulse length 6.0 µs) and a 10 s recycle delay. Sixty-four scans were accumulated at a MAS rotation frequency of 0.8 and 1.4 kHz. Tetramethylsilane was used for ¹H as reference standard.

Measurements were performed at temperatures between 102 and 425 K by heating/cooling the nitrogen gas flow. The temperature was estimated by a Cu-Constantan thermocouple placed in the nitrogen gas supply dewar at the bottom of the sample holder. Calibration of the sample temperature as well as an estimation of the temperature gradient along the sample was carried out by measuring the 207 Pb NMR signal of Pb(NO₃)₂ whose chemical shift shows a linear correlation as a function of temperature (Bielecki and Burum 1995). The maximum temperature gradient at the same temperature amounts to $\Delta T = \pm 3$ K along the sample.

The {'H} \rightarrow ¹⁵N CPMAS and ¹⁵N MAS 'H high-power decoupled NMR spectra were obtained at a transmitter frequency of 40.55 MHz using a standard 7 mm BRUKER MAS probe. For the cross-polarization the 90° pulse length for ¹H was 8.0 µs [v_{rt}(¹H) = v_{rt}(¹⁵N)_{solid} = 31.25 kHz]. The contact time was 5 ms in the experiment. It should be noted, that the CPMAS experiments are non-quantitative. The intensities depend greatly on the heteronuclear dipolar interaction parameters and the contact time. For the ¹⁵N MAS 'H high-power decoupled NMR spectra the pulse length for ¹⁵N was 4.0 µs. The recycle delay was 10 s for both experiments. A total of 32–128 scans were accumulated at a MAS rotation frequency of 1.0 kHz. A 1 *M* aqueous solution of ¹⁵NH₄¹⁵NO₃ was used as reference standard setting the NH₄ resonance to 0 ppm.

The static and MAS ¹H NMR lineshapes as well as the ¹⁵N MAS NMR lineshapes were fitted with chemical shift anisotropy lineshapes and Lorentzian lines using the DMFIT2005 program (Massiot et al. 2002). The spatial coordinates of the chemical shielding tensor σ in the principle-axis system are defined in such a way that the direction of the strongest absolute interaction is fixed as the z-direction. $\sigma_{z\sigma}$ $\sigma_{\gamma\gamma}$ and σ_{zz} are the principal elements of the tensor.

$$\sigma = \begin{pmatrix} \sigma_{xx} & 0 & 0 \\ 0 & \sigma_{yy} & 0 \\ 0 & 0 & \sigma_{zz} \end{pmatrix}, \quad \left| \sigma_{zz} - \sigma_{iso} \right| \ge \left| \sigma_{xx} - \sigma_{iso} \right| \ge \left| \sigma_{yy} - \sigma_{iso} \right|$$
(1)

Three parameters can be extracted from each CS lineshape in the NMR spectrum. The isotropic chemical shift δ_{iso} that is defined by the trace (*Tr*) of the symmetric chemical shielding tensor, the chemical shift anisotropy δ_{aniso} , which characterizes the difference between *z*-axis and *x*-*y* plane of the principle axis system and finally the asymmetry parameter η that describes the deviation from axial symmetry and can reach values between 0 and 1 (Spiess 1978).

$$\delta_{\rm iso} = \frac{1}{3} \, Tr \left\{ \sigma \right\} \tag{2}$$

$$\delta_{aniso} = \sigma_{zz} - \sigma_{iso} \tag{3}$$

$$\eta = \frac{\sigma_{yy} - \sigma_{xx}}{\sigma_{zz} - \sigma_{iso}}, 0 \le \eta \le 1$$

(4)

RESULTS AND DISCUSSION

Static ¹H and low-speed MAS NMR spectra of letovicite

Previous ¹H MAS NMR experiments showed that the signal of the ammonium protons and the two signals of the free protons of the ferro- and the paraphase of letovicite can be clearly distinguished by their different chemical shift (Fechtelkord et al. 2000). A significant change of the dynamics of the ammonium tetrahedra can be observed at approximately 397 K, which corresponds to a temperature well below the phase transition temperature of $T_c = 413$ K. The decrease of the lineshape-independent second moment M_2 of the NH₄ resonance is caused mainly by time-averaging of the homonuclear dipolar interactions between the ammonium protons. The ferroelastic domains of the letovicite are formed in this very temperature range, so that coupling between the dynamics of the ammonium tetrahedra and the formation of the domain walls is likely. In contrast to that behavior a strong motional increase of the free acidic protons is observed in the vicinity of T_c , which is indicated by the reduction of the signal half widths. Thus, the increase of the free proton dynamics accompanies the phase transition. Beyond that the increasing dynamics of the free protons is responsible for the proton conduction of the super-ionic phase with T_c in the *a-b* plane of the crystal.

To sum up, the ¹H MAS NMR experiments are able to give information about changes in the dynamics of the protons. However, they cannot identify the type of motion. For this reason, supporting static variable-temperature ¹H and low-speed MAS NMR experiments of letovicite were carried out. The complete chemical shift anisotropic interaction is apparent in the static spectrum, where variable temperature experiments can provide information about the motional behavior of the protons and their local environments.

The static ¹H NMR spectra (Fig. 1) essentially confirm the results of the recent ¹H MAS NMR experiments. As described in Fechtelkord et al. (2000) only the broad signal of the ammonium proton can be observed in the static measurements at the beginning (room temperature) due to the strong homonuclear dipolar interactions. Distinct signals of the free protons are not visible, because they are located in SO-H…OS bonds in the center of the sulfate double layers and at room temperature they are nearly static. This causes broad resonances, which cannot be resolved from the strong ammonium signal. With rising temperature the proton dynamical rate increases and thus their resonances become narrower. This leads to the fact that the H1 resonance of the free protons becomes visible starting at 350 K at a signal position of approximately 14 ppm. Starting from 390 K (375 K in the MAS spectrum) the second signal of the free protons of the paraphase can be observed at approximately 13 ppm. Increasing the temperature steadily the H1 signal of the free protons loses intensity and disappears completely at higher temperatures, while the H2 signal becomes more intense. The coexistence range of ferro- and paraphase can only be detected in a smaller temperature range (390 to 405 K) compared to the



FIGURE 1. Static ¹H NMR spectra of the ammonium signal of letovicite in the temperature range of 293–420 K.

MAS experiments (375 to 420 K).

For further evaluation of the static ¹H NMR experiments the spectrum at a temperature of 400 K (Fig. 2) was selected since at this temperature both free proton signals are present. Using the estimated ¹H isotropic chemical shifts of the free proton signals from ¹H MAS NMR spectra [δ_{iso} (H1) = 14.5 ppm, δ_{iso} (H2) = 13 ppm] it was possible to fit these signal parts applying a chemical shift anisotropy (CSA) lineshape and to determine the chemical anisotropy (δ_{aniso}) as well as the asymmetry parameter (η) of the signals of the free protons (Table 1). Since the signal intensities of the free protons are very low compared to the total signal area, supplemental variable temperature ¹H MAS NMR experiments with low-spinning frequencies (0.8 and 1.4 kHz) were acquired. At low rotational frequency the chemical shift anisotropic interaction is only partly averaged, so that the numerous sidebands contain the chemical shift anisotropy information. Figure 3 shows an example of the 1H MAS NMR experiment at a rotational speed of 1.4 kHz and T = 400 K.

Our MAS experiments at low rotational frequency confirm the lineshape simulation fit of the free proton signals, the chemical anisotropy and asymmetry parameters (Table 1) already estimated from the static spectra.

The asymmetry parameter of the H1 signal amounts to $\eta = 1.0$ and is reduced to $\eta = 0.0$ for the H2 signal. The decrease of η to zero gives evidence that the local chemical environment of the free protons changes during the phase transition from the ferro- to the paraphase. During the phase transition the symmetry increase



FIGURE 2. Experimental signal and spectral fit of the static ¹H NMR experiment at T = 400 K.

TABLE 1.Chemical shift parameters of the 'H signals of the free acidic
protons from the static 'H NMR- and low-speed MAS 'H
NMR-spectra at T = 400 K

| | | H1 | | | H2 | |
|---|------------------|------------------|--------|------------------|--------------------|--------|
| | δ _{iso} | δ_{aniso} | η | δ _{iso} | δ _{aniso} | η |
| MAS 1.4 kHz | 14.2(1) | 8.5(5) | 0.9(2) | 13.2(1) | 4.5(5) | 0.0(2) |
| MAS 0.8 kHz | 14.1(1) | 8.4(5) | 0.9(1) | 12.9(1) | 3.5(5) | 0.0(3) |
| static | 14.1(2) | 8(2) | 1.0(2) | 13.3(4) | 3(2) | 0.1(5) |
| <i>Note:</i> The ¹ H chemical shift of the ammonium resonance is at 7.0 ppm. | | | | | | |

takes place in such a manner that the local symmetry of the free protons at the 2h Wyckoff site (center of the hydrogen bond) in the monoclinic phase increases to a dynamically disordered distribution at the 9e Wyckoff position in the trigonal modification (Schwalowsky et al. 1998).

Comparing the chemical shift anisotropy of the free proton signals of the ferro- and paraphase it is noticed that δ_{aniso} of the paraphase signal is half as great as that of the ferrophase. This is due to the expected faster motion of the free protons in the trigonal phase. Schmidt-Rohr and Spiess (1994) showed that a jump of a proton between two crystallographic sites can reduce the chemical shift anisotropy to one-half, if this two-site jump includes an angle within the range of 70.5 to 109.5° between the two main directions of the chemical shift tensors. On the basis of the interbond dynamics of the disordered dynamical hydrogen bond network (DDHBN) theory the sulfate tetrahedra start to rotate about their threefold axis with increasing temperature. During the rotation of the sulfate tetrahedra in the interbond mechanism the hydrogen bond is disconnected and the free proton is transported to the next free site. Finally, a new hydrogen bond forms. This transport of the proton represents a two-site jump related to Schmidt-Rohr and Spiess (1994). The angle between the two main directions of the chemical shift tensors amounts to $\alpha = 105.1^{\circ}$ (Sooryanarayana and Row 1996) and is in the range from 70.5 to 109.5°, mentioned above. The decrease of the chemical shift anisotropy of the free proton signal to one-



FIGURE 3. Experimental signal and spectral fit of the ¹H MAS NMR experiment at T = 400 K and a rotational frequency of 1.4 kHz.

half during the phase transition thus supports the DDHBN theory described by Merinov (1996).

¹H MAS and static NMR investigations can only give information about the change of dynamical processes, but not about the motional type. As a better tool to deal as a particularly sensitive probe of motional mechanism static solid-state ²H NMR spectroscopy is used in part II of this work.

¹⁵N MAS (CPMAS) NMR spectra of letovicite

In addition to the ¹H NMR-experiments ¹⁵N MAS NMR experiments of partially deuterated ¹⁵N-enriched letovicite with a low rotational frequency of 0.5 kHz were carried out. ¹⁵N is an isotope with a nuclear spin of I = 1/2, so that chemical shift anisotropy and dipole interactions can be averaged by the MAS technique. In this way, the signal line width can be reduced significantly. However, a low rotational frequency is applied to ensure that the rotational sidebands resulting are able to supply important additional information about the dynamics of the NH₄ tetrahedra. The ¹⁵N MAS NMR spectra were acquired using highpower broadband decoupling and/or cross-polarization. Dipolar coupling to protons is reduced and cross-polarization achieves a better signal/noise ratio at the same time. These experiments are able to distinguish the individual nitrogen signals according to their crystallographic sites.

The ¹⁵N NMR spectra were measured within a range from 215 to 420 K. In this temperature range, letovicite undergoes several phase transitions depending on the deuteration grade (Osaka et al. 1980). The partially deuterated sample examined here has a deuteration grade of $59 \pm 7\%$. Thus, the corresponding temperature for the ferroelastic to paraelastic phase transition is $T_C = 408$ K.

At low temperatures, three different nitrogen signals can be observed in the ¹⁵N MAS NMR spectra in Figure 4 at δ_{iso} = 3.5 ppm, -0.6 ppm, and -1.8 ppm for the N(I), N(II), and N(III) signals, respectively. In this temperature range letovicite possesses



FIGURE 4. Single-pulse ¹⁵N MAS NMR spectra with ¹H high-power decoupling of the letovicite ammonium signal in the temperature range of 215–420 K. {¹H}¹⁵N CPMAS NMR spectra are marked with asterisks.

the space group symmetry *P2/n* or *Pn*. The N(III) signal at –1.8 ppm moves with increasing temperature toward the N(II) resonance position at –0.6 ppm. Moreover, all signals show a small shift to higher frequencies with increasing temperature (Fig. 4). Above 265 K, the signals N(III) and N(II) overlap to a single N(II*) signal at $\delta_{iso} = 0.5$ ppm; the crystal undergoes a phase transition to the monoclinic space group *C2/c*. In addition, at increasing temperatures the N(I) and N(II*) signals shift together to one N(I*) signal, too (Fig. 4). The frequency shift of the ¹⁵N resonances continues to tend to higher ppm values. Above *T* = 420 K only one nitrogen signal at 3.3 ppm is present while the crystal now shows space group symmetry $R\overline{3}m$. All shift changes as function of temperature are displayed in Figure 5.

At low temperatures, three signals [N(I), N(II), and N(III)] can be observed due to the three crystallographically different nitrogen positions in the primitive lattice. These three positions are approximately occupied equally since the integrated signal area in each case is one third of the total area. With increasing temperature, the N(III) and N(II) signals shift and at 265 K only a single N(II*) signal remains. The integrated signal area below the N(II*) signal is now twice as large as that below the former N(I) signal, which corresponds to a distribution of nitrogen positions of approximately 2:1. Thus, the N(I) signal can be assigned to the nitrogen atoms of the N(1)H₄ tetrahedra within the sulfate double layer, while the N(II) and N(III) resonances originate from the two N(2)H₄ ammonium tetrahedra of the NH₄ double layer. Moreover, the isotropic chemical shift of the signals gives evidence for that signal assignment. The direct neighborhood of the N(1) atoms to the oxygen atoms of the sulfate tetrahedra



FIGURE 5. Isotropic chemical shift of the ¹⁵N MAS NMR resonances as a function of temperature.

leads to a changed electron distribution in the nitrogen electron shell induced by the strong oxygen polarity and thus a changed isotropic chemical shift compared to NH_4^+ cations in solution (0 ppm). On the other hand, the NH_4 tetrahedra of the double layers experience almost no influence of other neighboring atoms and therefore behave like ammonium tetrahedra in solution with $\delta_{iso}=0.5$ ppm.

The superposition of the N(II) and N(III) resonances results from the symmetry increase of the crystal lattice with increasing temperature. The symmetry changes from a primitive *P* lattice to a *C*-centered lattice, so that the local coordination spheres of the N(2)H₄ tetrahedra become identical, and thus also their isotropic chemical shift. Accordingly only one N(II*) signal of the previous two ammonium tetrahedra remains.

At room temperature, the protons of the ammonium group undergo fast rotational processes (Totz et al. 2001). The motion can be described best by a "fast" dynamic reorientation (10⁻⁸ s) of the tetrahedra leading to the dynamically averaged chemical shift anisotropy at room temperature. It can be noticed that at a rotational frequency of 500 Hz nearly no rotational sideband intensity can be observed and thus a very low chemical shift anisotropy results. This prevents a further evaluation of the ¹⁵N MAS NMR spectra regarding the motional behavior of the ammonium tetrahedra, since the nearly isotropic proton environment of the nitrogen (ideal tetrahedral coordination) makes a variable temperature analysis of the chemical shift anisotropy of the signals impossible.

The N(I) signal and the N(II*) signal shift together on further increase of temperature, and above 420 K a single N(I*) signal for all NH₄ tetrahedra is present. By the increase of temperature a symmetry change of the structure takes place to space group $R\overline{3}m$. In addition, the dynamics of the ammonium tetrahedra increases in rate with the increasing temperature. Above T_C a fast dynamics of all anions and cations is present, and therefore we see a time-averaged environment of both the sulfate anions as well as the ammonium tetrahedra. The chemical shift tensors of the different nitrogen atoms are time-averaged to the same isotropic value, so that the individual nitrogen positions cannot be distinguished. Due to the open crystal structure the SO₄ groups possess a high freedom to perform thermally induced torsional oscillations and reorientations so that at high temperatures the two remaining N sites experience the same time-averaged chemical environment and consequently the same time-averaged chemical shift tensor. The two nitrogen signals thus merge into one signal located at a time-averaged resonant frequency. Dolinšek et al. (1998) found similar results in their ⁸⁷Rb NMR study for the Rb sites in Rb₃H(SO₄)₂.

The shift of all signals to higher frequencies (Fig. 5) is caused partially by the thermally induced lattice expansion. This should induce a resonance shift change. However, another effect at higher temperatures is the changing diamagnetism of both the sample and the probehead. Thus, a change of the static magnetic field line density over the sample takes place inducing a changed resonance frequency.

The additional low intensity signal at T = 420 K at approximately 1 ppm is due to the beginning letovicite decomposition and can be assigned to ammonia (NH₃).

To sum up, the ¹⁵N MAS NMR spectra reflect the symmetry changes of the structure reasonably well. The shift of signals can be directly attributed to the phase transitions of letovicite. At high temperatures it additionally shows the time-averaging of the chemical shift tensor caused by strong dynamics of the NH₄ tetrahedra as well as their local environment.

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