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To cite this article: Yu N Ivanov *et al* 1999 *J. Phys.: Condens. Matter* **11** 3751

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Chemical exchange in NH_4HSeO_4 single crystals studied by two-dimensional ^2H nuclear magnetic resonance

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Received 4 December 1998

Abstract. Processes of chemical exchange of deuterons in partially deuterated ammonium hydrogen selenate, NH_4HSeO_4 (AHSe), crystals are investigated by means of ^2H nuclear magnetic resonance (NMR) experiments over a wide temperature range. The temperature dependencies of the quadrupole line splittings in the one-dimensional spectra of AHSe above 350 K revealed line-shape changes which are characteristic for chemical exchange processes. A detailed study of these exchange processes in AHSe is achieved by means of two-dimensional ^2H NMR experiments. In the temperature range investigated, a chemical exchange occurs only between those deuteron (proton) sites which are involved in hydrogen bonds (α - and β -positions). It was established that the rates of exchange between all types of hydrogen-bound deuteron are approximately the same. Exchange between these positions and the deuterons in the ND_4 groups could not be detected. On the basis of our findings, we finally discuss a model for the microscopic mechanism of hydrogen transport in AHSe.

1. Introduction

Ammonium hydrogen selenate NH_4HSeO_4 (AHSe) belongs to a group of crystals in which the appearance of the ferroelectric state is connected with proton ordering in the hydrogen bond system. The most interesting features of this crystal are the existence of an incommensurate phase [1, 2] and the observation of protonic conductivity [3–5]. The following sequence of phase transitions is observed in AHSe under the condition of continuous temperature change [6–8]: low-temperature phase ($T_{C2} = 98$ K)—ferroelectric phase ($T_{C1} = 250$ K)—incommensurate phase ($T_I = 261$ K)—paraelectric phase ($T_{SI} = 417$ K)—high-temperature superionic phase. The crystal structure of the paraelectric phase is monoclinic with six formula units per unit cell, $Z = 6$ [9]. The structural framework (figure 1) is formed by selenate ions bound by hydrogen bonds in infinite chains along the ferroelectric b -axis. The ammonium ions bind the selenate ions along the two other axes, a and c .

Previous studies [1, 3] of ^1H NMR spectra, nuclear spin-relaxation times and conductivity measurements in the close vicinity of T_{SI} suggest that the diffusion of both protons and NH_4^+ cations is isotropic. According to the ^{77}Se NMR data it was suggested [3–5] that the mechanism of protonic transport consists in correlated reorientations of the selenate groups and a subsequent transfer of the hydrogen bond protons from one chain of the selenate groups to another, and that the activation energy of the reorientation is a limiting factor of the proton

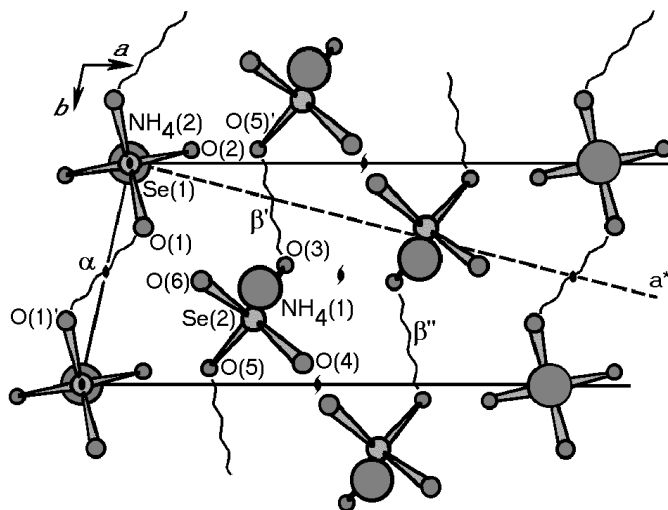


Figure 1. The structure of NH_4HSeO_4 in the paraelectric phase. Only half of the unit cell is shown. Hydrogen bonds connecting the oxygen atoms of SeO_4 groups are represented by the wavy lines.

hopping. It should be noted, however, that the ^1H NMR investigations resulted only in the description of some ‘average’ behaviour of both sorts of proton belonging to the H bonds and NH_4 groups and could not provide evidence for the microscopic mechanism of the conductivity. For this reason we applied the powerful tool of one- and two-dimensional deuterium (^2H) NMR measurements to partially deuterated AHSe single crystals.

Quadrupole-perturbed ^2H NMR experiments are a very appropriate tool for investigating the local behaviour of the deuterons due to the direct relationship between the quadrupole line separation $\nu_2 - \nu_1$ and the electric field gradient tensor (EFG) element V_{zz} in the laboratory frame according to

$$\nu_2 - \nu_1 = \frac{6eQ}{4h} V_{zz}^{LAB} = \Phi_{zz}. \quad (1)$$

For the sake of simplicity we use the quantity Φ_{zz} (in units of Hz) instead of V_{zz} . Applying the well-known Volkoff formalism [10], which relates the tensor elements in the crystal frame with the line splitting measured, the EFG tensors in the crystallographic axes system (CAS) were determined for AHSe. Our tensors obtained for the deuterons in the proton bonds confirm previous results [11]. Moreover, we observed a quadrupole splitting also for the ammonium groups, and two different tensors could be determined at room temperature and at 390 K. Furthermore, the temperature dependencies of the quadrupole line splitting in the 1D NMR spectra above 350 K revealed changes which are characteristic for chemical exchange processes. Therefore, the aim of the investigations reported in this paper is a detailed study of the hydrogen mobility in partially deuterated AHSe crystals by means of one- and two-dimensional ^2H NMR experiments.

2. Experimental procedure

Partially deuterated (25%) ammonium hydrogen selenate crystals were grown from solutions with heavy water. In this process a deuteration not only of the bridging atoms, but also in the ammonium groups was achieved.

The NMR experiments were run at a resonance frequency of 46.073 MHz using a BRUKER MSL 300 NMR spectrometer. Excitation of the complete 1D NMR spectrum was achieved with a pulse duration of 4 μs . To avoid the influence of the dead time in the 1D spectra, a quadrupole spin-echo sequence was employed with a pulse distance of 25 μs . Furthermore, proton decoupling was applied to suppress the broadening of the ^2H NMR lines due to dipolar interaction between the deuterons and the remaining protons. The repetition time was chosen between 10 s and 15 s.

2D ^2H NMR exchange experiments were carried out by means of the following echo sequence: $(\pi/2)_x-t_1-(\pi/2)_{-x}-\tau_m-(\pi/2)_x-\tau-(\pi/2)_y-\tau-t_2$. The values t_1 , t_2 , τ and τ_m denote the evolution time, acquisition time, pulse distance and mixing time, respectively. A duration of 25 μs was chosen for τ .

3. Results and discussion

3.1. Interpretation of the one-dimensional ^2H NMR spectra of AHSe

The basis of our studies on the partially deuterated AHSe samples consists in the interpretation of the 1D ^2H NMR spectra. Typical spectra for AHSe depending on the temperature in the range between room temperature and 410 K are displayed in figure 2. These spectra were acquired in an orientation where the a^* -axis is perpendicular to the external magnetic field B_0 and the angle between the B_0 -field and the b -axis is 30° . In this orientation three line doublets can be observed, i.e. one central doublet and two doublets with frequency splittings larger than 60 kHz. From the rotation patterns for the orientations where the a^* -, b - and c -axes are perpendicular to the field and where the crystal is rotated around these axes (not shown here), respectively, we find a very weak angular dependence for the central line. The dependencies for the other two lines correspond to previous data on the deuterons in the H bonds in special (α -)

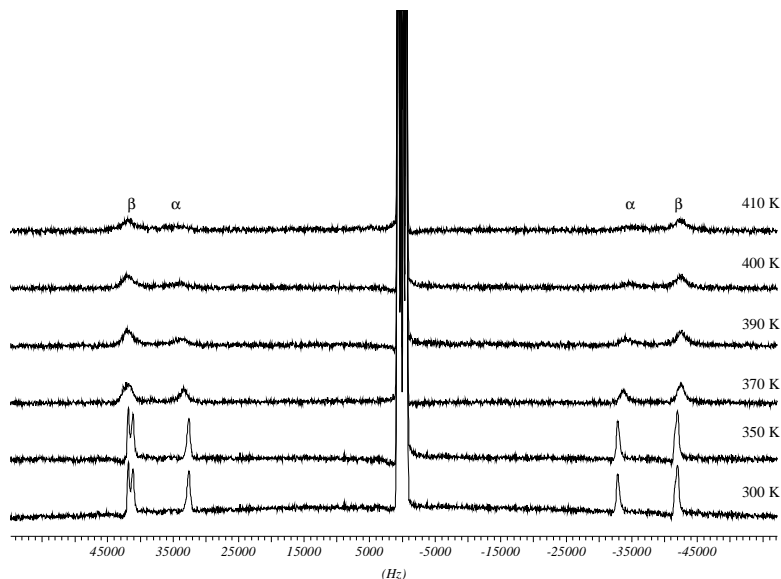


Figure 2. Typical temperature dependence of the quadrupolar line splitting in NH_4HSeO_4 . An orientation for the crystal was chosen such that the a^* -axis is perpendicular to the external magnetic field. The b -axis and the direction of the field include an angle of 30° .

and general (β -) lattice positions. The central line doublet can be assigned to the ammonium group, and its angular dependence, which is observed in our studies for the first time, will be discussed in section 3.4.

From the temperature-dependent measurements (figure 2) it follows that no change in the line shape is observed at temperatures from 300 K to ≈ 350 K. Above 350 K broadenings of those lines can be observed which are assigned to the α - and β -positions in the hydrogen bonds. Up to a temperature of 410 K a different dependence of the linewidths of the α - and β -deuterons on temperature can be inferred from the spectra. This behaviour points towards the presence of chemical exchange processes, but from these spectra no exact conclusion can be reached about the exchanging positions and the exchange rates.

For the further interpretation of the observed NMR spectra, i.e. the broadening of lines, we have to consider the exchange dynamics. The chemical exchange between different positions i and j is characterized by the transition probabilities (exchange rates) p_{ij} , denoting the number of deuterons moving from site i to site j per unit time. With the different p_{ij} the rate matrix p is established, describing the dynamics of the exchange process. As is well known (cf. e.g. Abragam [12]), the description of exchange processes is achieved by the following master equation:

$$\frac{dn_i}{dt} = \sum_j^n p_{ij} n_j \quad (2)$$

or in matrix notation $\dot{\mathbf{n}} = \mathbf{p}\mathbf{n}$.

Here, the quantities n_i are the occupation numbers of the sites i .

The solution of equation (2) is

$$\mathbf{n}(t) = \exp(\mathbf{p}t)\mathbf{n}_0 = \mathbf{A}(t)\mathbf{n}_0. \quad (3)$$

Here $\mathbf{n}(t) = \{n_1, \dots, n_i\}$ is the vector describing the population numbers of the deuterons at the sites at the time t . The vector $\mathbf{n}_0 = \{n_{01}, \dots, n_{0i}\}$ contains the respective numbers of deuterons at the sites at the time $t = 0$, and \mathbf{A} is the exchange matrix with the elements a_{ij} .

Our aim is to determine the number of exchanging deuteron sites and their exchange rates. In order to differentiate between the deuterons taking part in the exchange processes we suggest performing two-dimensional exchange experiments.

3.2. Two-dimensional ^2H NMR exchange experiments

We follow the known approach [13, 14] to obtain the elements a_{ij} of the exchange matrix by means of two-dimensional exchange experiments and to calculate the p_{ij} . Taking into account the inequality $T_2 \ll \tau_m \ll T_1$ applying to the transverse relaxation time T_2 , the mixing time τ_m and the longitudinal relaxation time T_1 , which holds for our experiments, no further relaxation effects have to be considered. The intensities I_{ij} observed in the 2D ^2H NMR spectra at a mixing time τ_m are then directly proportional to the number of deuterons exchanging from site i to site j , which is characterized by n_{ij} . The elements of the exchange matrix \mathbf{A} are connected to the intensities I_{ij} in the 2D spectra according to

$$I_{ij} \sim A_{ji} n_i \quad (4)$$

where n_i denotes the occupation number of site i .

In order to investigate the exchange processes in the case of low exchange rates, i.e. if the exchange rate is much less than the quadrupolar splitting, 2D ^2H NMR exchange experiments were performed in the temperature range between 300 K and 350 K. A typical two-dimensional ^2H NMR spectrum of AHSe is shown in figure 3 for an orientation where the a^* -axis is

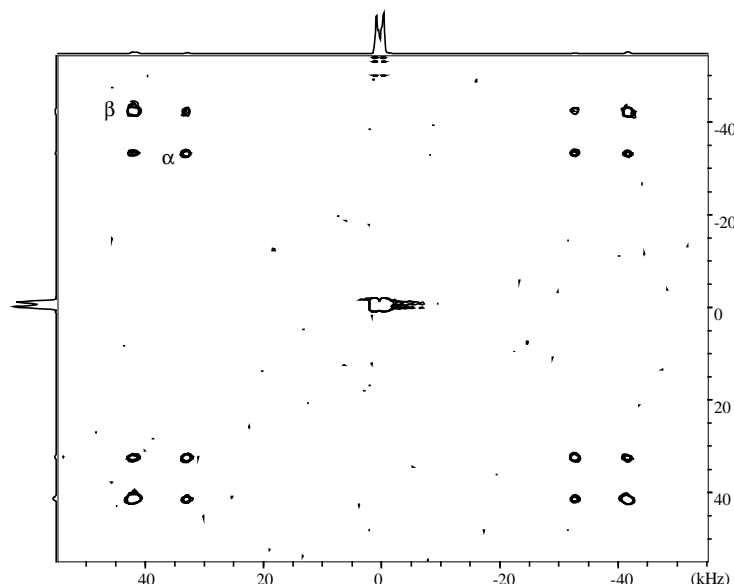


Figure 3. A typical 2D ^2H NMR exchange spectrum for NH_4HSeO_4 (25% deuterated) at 350 K at a mixing time of 3 ms. The a^* -axis is perpendicular to the direction of the external magnetic field. The b -axis and the external field include an angle of 30° . Exchange processes are characterized by the occurrence of off-diagonal peaks.

perpendicular to the external magnetic field. The angle between the direction of B_0 and the b -axis was chosen to be $\approx 30^\circ$, in order to ensure a sufficient separation of the α - and β -lines as well as a relatively small spectral width of ≈ 100 kHz. The spectrum of figure 3 was acquired at a temperature of 350 K at a mixing time of 3 ms.

Typical off-diagonal peaks occur in the spectra at 350 K and at lower temperatures (where in the 1D spectra an exchange process is no longer observable), which allows the study of the exchange processes. In the case of AHSe it is obvious from figure 3 that the exchange occurs between the α - and β -positions of the hydrogen bonds, but not between these positions and the deuterons in the ammonium groups. Even for a 2D spectrum measured at 390 K and with a rather long mixing time of 10 ms, no cross peaks for the above-mentioned positions were detectable. Therefore, in the experimentally accessible temperature range, we can exclude any exchange between the deuterons in the ammonium groups and in the hydrogen bonds, and we only have to deal with a two-site exchange between the α - and β -positions.

This implies a size of our exchange and rate matrices of 2×2 . Consequently, we can explicitly formulate equation (2) in the following way:

$$\begin{pmatrix} \dot{} \\ n_1 \\ \dot{} \\ n_2 \end{pmatrix} = \begin{pmatrix} -p_{12} & p_{21} \\ p_{12} & -p_{21} \end{pmatrix} \begin{pmatrix} n_1 \\ n_2 \end{pmatrix}. \quad (5)$$

Here we had to assume two different exchange rates p_{12} and p_{21} , as implied by the two different occupation numbers for the α - and β -positions. They are connected via the equation

$$\frac{n_1}{n_2} = \frac{p_{21}}{p_{12}}. \quad (6)$$

According to equation (3) the exchange matrix \mathbf{A} is calculated to be

$$\mathbf{A}(t) = \frac{1}{1 + p_{12}/p_{21}} \times \begin{pmatrix} 1 + (p_{12}/p_{21}) \exp(-(p_{12} + p_{21})t) & 1 - \exp(-(p_{12} + p_{21})t) \\ (p_{12}/p_{21})[1 - \exp(-(p_{12} + p_{21})t)] & (p_{12}/p_{21}) + \exp(-(p_{12} + p_{21})t) \end{pmatrix}. \quad (7)$$

Now the two different exchange rates may be calculated using the two ratios between off-diagonal and diagonal elements of \mathbf{A} .

In order to confirm the intensity ratio of $n_1/n_2 = 1/2$, which is given for the α - and β -positions by the structure of AHSe but would not hold in the case of unequal deuteration (non-statistical deuteron distribution), we acquired a set of 2D spectra at 350 K depending on the mixing time. For mixing times of 3, 9 and 15 ms the intensity ratios A_{12}/A_{11} and A_{21}/A_{22} were calculated. Figure 4 displays the ratio A_{12}/A_{11} as a function of the mixing time and the fit of this dependence to the theoretical ratio

$$A_{12}/A_{11} = (p_{12}/p_{21})[1 - \exp(-(p_{12} + p_{21})t)]/[1 + (p_{12}/p_{21}) \exp(-(p_{12} + p_{21})t)]. \quad (8)$$

It is apparent from this figure that within the experimental error we can confirm the ratio of 1:2. This finding corresponds to equal deuteration of the α - and β -positions. Therefore, our exchange matrix takes the simpler form

$$\mathbf{A} = \frac{1}{3} \begin{pmatrix} 1 + 2 \exp(-3pt) & 1 - \exp(-3pt) \\ 2 - 2 \exp(-3pt) & 2 + \exp(-3pt) \end{pmatrix}. \quad (9)$$

The two exchange rates $p_{12} = 2p_{21} = 2p$ may now be calculated using the peak ratios from matrix (9). For the determination of the rate matrix at a fixed temperature, one 2D experiment is sufficient, provided that a suitable mixing time is chosen. The mixing time was set according to the expected rate, whose order of magnitude could be estimated from the 1D

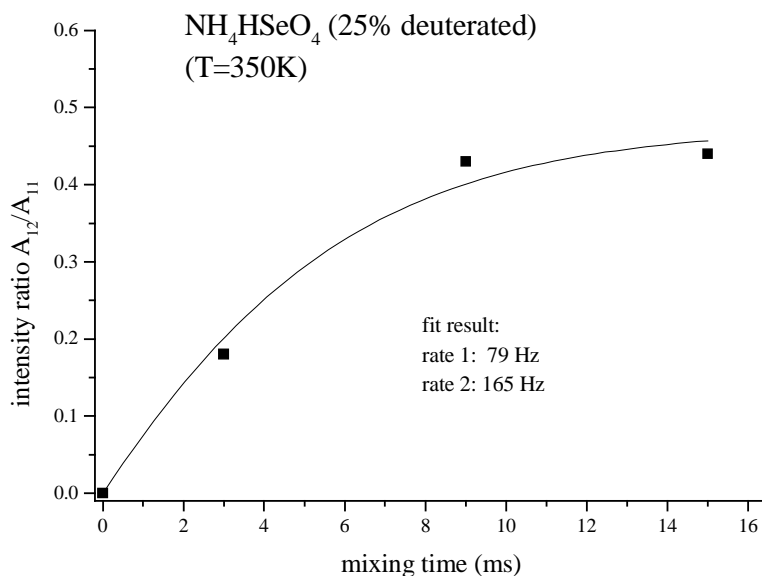


Figure 4. The intensity ratio A_{12}/A_{11} of off-diagonal-to-diagonal peaks versus the mixing time. The best fit of the model of equation (7) gives values for the two rates of 79 Hz and 165 Hz.

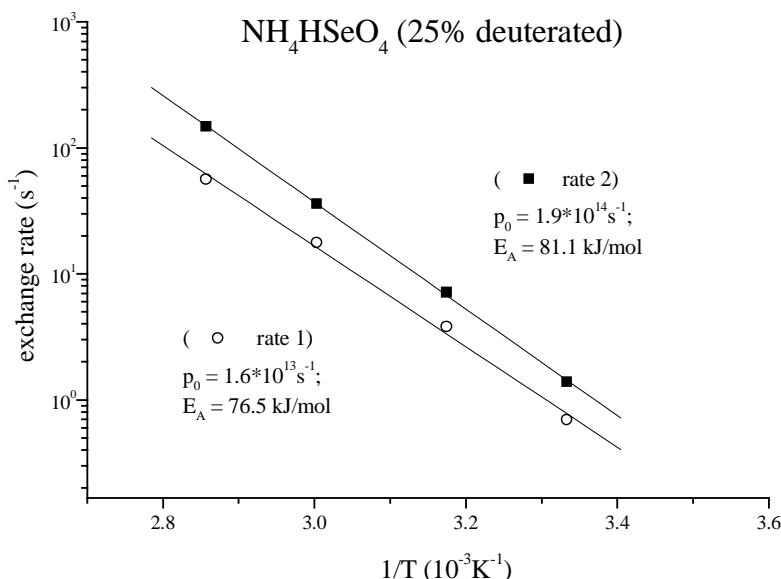


Figure 5. Exchange rates versus reciprocal temperature for NH_4HSeO_4 .

line-shape variations. In the case of our AHSe crystals, the rate matrix was determined for four different temperatures (300, 315, 333 and 350 K) in the experimentally accessible range of the 2D NMR experiments (≈ 300 K to 355 K).

In figure 5 the rates obtained are plotted versus the reciprocal temperature in an Arrhenius representation. Both rates were calculated by means of the above formulae, and we achieved a fairly good correspondence to the expected ratio of 1:2. The rates were fitted to an Arrhenius equation with an activation energy E_a :

$$p(T) = p_0 e^{-E_a/RT}. \quad (10)$$

The activation energies E_a are nearly equal ($\approx 80 \text{ kJ mol}^{-1}$). They are in agreement with the expected range of values for deuteron jumps in crystals with hydrogen bonds, e.g. like in betaine compounds such as betaine phosphate (83 kJ mol^{-1}) and others [15]. For the pre-exponential factors p_0 , we find values of $1.6 \times 10^{13} \text{ s}^{-1}$ and $1.9 \times 10^{14} \text{ s}^{-1}$. The order of magnitude of these data is potentially of interest for the comparison of these results with conductivity measurements, which are still in progress. It has been shown recently for the mixed crystal system of deuterated betaine phosphate/phosphite [15, 16] that by means of establishing a relationship between chemical exchange and conductivity processes new findings on the charge carriers in systems with ionic conductivity can be obtained.

3.3. Deuteron exchange between the different β -positions

In the case of the 2D experiments discussed in the previous section, our ^2H NMR experiments usually cannot distinguish between the different β -positions in the unit cell. If, however, we select a different orientation, in which the b -axis is perpendicular to the B_0 -field, two magnetically non-equivalent β -positions are present. To decide whether a chemical exchange also occurs between these different β -positions (denoted as β' and β''), an additional 2D experiment was performed in a suitable orientation. For the 2D spectrum of figure 6 an angle of $\approx 15^\circ$ between the a^* -axis and B_0 was chosen. As can be seen from the figure, the two

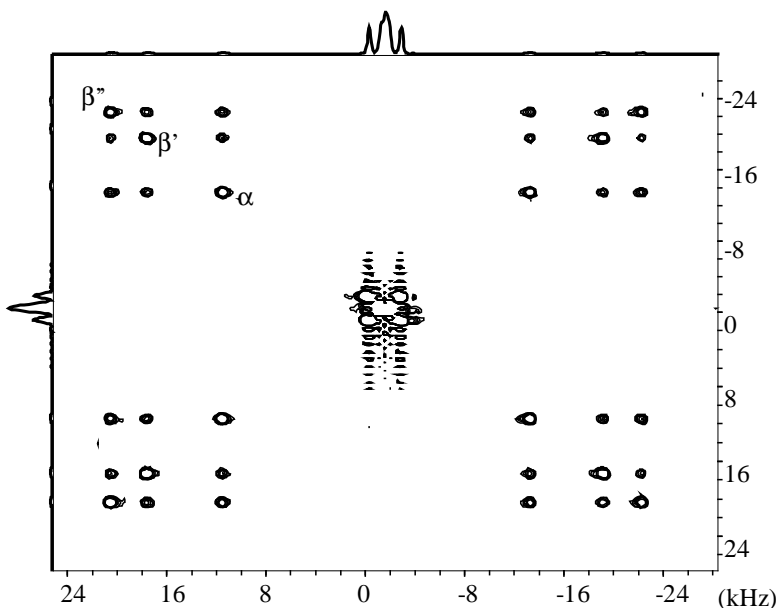


Figure 6. A 2D ^2H NMR exchange spectrum for NH_4HSeO_4 (25% deuterated) at 350 K at a mixing time of 3 ms. In this orientation the b -axis is perpendicular to the direction of the external magnetic field. The a^* -axis and the external field include an angle of 15° . Exchange processes characterized by off-diagonal peaks also occur between the two different β -positions.

spectroscopically distinguishable β -positions appear within a spectral width of ≈ 50 kHz. This spectrum, measured at a mixing time of 3 ms, also exhibits cross peaks for the magnetically non-equivalent β' - and β'' -positions. Thus we conclude that there is also an exchange between the deuterons in these positions.

As can be inferred from the nearly equal intensities of the respective cross peaks, approximately equal α - β' , α - β'' and β' - β'' exchange rates are suggested. This suggestion completely accords with the equal occupation numbers of the β' -, β'' - and α -positions.

3.4. The behaviour of the ND_4 groups

As mentioned in the first section, the central-line doublet can be assigned to the ammonium group. Due to the application of proton decoupling in our ^2H NMR experiments, we are able to achieve a rather high resolution for this central area, revealing its composition of actually more than one doublet. From the angular dependence at temperatures of 300 K and 390 K, two different electric field (EFG) tensors were determined in each case. One of these tensors is nearly an axially symmetric tensor which belongs to the ammonium groups $\text{NH}_4(2)$ at the special position. The other EFG tensor can be assigned to the ammonium group $\text{NH}_4(1)$ at a general position. It can be seen from table 1 that with increasing temperature only a slight change of the tensor elements occurs. Thus our finding provides evidence that no noticeable exchange effects are present for the ammonium groups. This result is in contradiction to previous assumptions [3], where a fast diffusive motion between all ammonium positions was proposed on the basis of the analysis of ^1H NMR spectra at 390 K. Consequently, by means of our ^2H NMR investigations we can refute this earlier assumption.

Table 1. EFG tensors of the different ammonium groups at temperatures of 300 K (top) and 390 K (bottom).

	$\text{NH}_4(2)$				$\text{NH}_4(1)$		
	a^*	b	c		a^*	b	c
$Q_{11} = -1350$ kHz	0	0	1	$Q_{11} = -1196$ kHz	0.51	0.77	± 0.39
$Q_{22} = -1329$ kHz	± 0.73	± 0.68	0	$Q_{22} = -402$ kHz	± 0.4	± 0.61	-0.68
$Q_{33} = 2679$ kHz	± 0.68	0.73	0	$Q_{33} = 1598$ kHz	0.76	-0.19	± 0.62
	$\text{NH}_4(2)$				$\text{NH}_4(1)$		
	a^*	b	c		a^*	b	c
$Q_{11} = -850$ kHz	0	0	1	$Q_{11} = -920$ kHz	0.26	0.93	0.81
$Q_{22} = -1306$ kHz	± 0.72	± 0.69	0	$Q_{22} = 519$ kHz	-0.47	0.35	0.81
$Q_{33} = 2157$ kHz	± 0.69	0.72	0	$Q_{33} = 1439$ kHz	0.84	-0.09	0.53

4. Conclusions

On the basis of the results discussed in the previous sections we propose the following microscopic mechanism of hydrogen exchange. In the temperature range investigated a chemical exchange occurs only between those deuterium (proton) sites which are involved in hydrogen bonds (α - and β -positions). An exchange between these positions and the deuterons in the ND_4 groups could not be detected. The obvious differences between the magnitudes of the splittings for the ^2H NMR line doublets belonging to α - and β -deuterons on one hand and to deuterons in the ammonium groups on the other hand clearly reveal a fast reorientation of the latter group. The small line splitting for the ND_4 groups apparently reflects non-cubic effective symmetry due to the monoclinic crystal symmetry. The chemical exchange between deuterons (protons) belonging to H bonds is characterized by deuterium jumps from α -positions to the different β -positions, i.e. from one chain to another. This is shown by two independent measurements. In crystal orientations where the lines of the two magnetically different β -deuterons coincide we observe two different exchange rates, i.e. a superposition of two exponential functions in the mixing curves. Here the ratio of the time constants is given by the ratio of the respective numbers of α - and β -deuterons (1:2). In another crystal orientation where the two β -deuterons are spectroscopically distinguishable, only one time constant can be measured, i.e. the rates of exchange between all types of hydrogen-bound deuterium are approximately the same. Hence, the deuterium hopping is not necessarily limited to the one-dimensional chains and does not necessarily require a fast reorientation of the SeO_4 groups as claimed previously. Consequently, from a microscopic point of view no anisotropy of deuterium motion is expected.

Acknowledgment

The financial support of the Deutsche Forschungsgemeinschaft is gratefully acknowledged.

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