Appl. Magn. Reson. 28, 431–440 (2005)

**Applied Magnetic Resonance**

# Chemical Exchange in $KHSeO_4$ and $NH_4HSeO_4$ Studied by Two-Dimensional NMR

**Yu. N. Ivanov**[1], **A. A. Sukhovsky**[1], **I. P. Aleksandrova**[1], and **D. Michel**[2]

[1] L.V. Kirensky Institute of Physics, Russian Academy of Sciences, Krasnoyarsk, Russian Federation
[2] Fakultät für Physik und Geowissenschaften, Universität Leipzig, Leipzig, Germany

Received August 18, 2004; revised January 27, 2005

**Abstract.** The microscopic mechanism of proton transport in partially deuterated potassium hydrogen selenate (KHSe) and in partially deuterated ammonium hydrogen selenate (AHSe) were studied by means of one-dimensional Fourier transform $^2H$ nuclear magnetic resonance (NMR), two-dimensional $^2H$ NMR and dielectric measurements over a wide temperature range. In both systems, KHSe and AHSe, the slow chemical exchange processes of deuterons between different hydrogen bridges occur. It was established that the rates of exchange between deuteron sites, which are involved in infinite chains of hydrogen bonds, are approximately the same for both crystals. The rates of exchange between these positions and the deuterons in the dimer groups of KHSe are approximately hundred times more slowly. On the basis of our findings, we discuss the models of the microscopic mechanism of hydrogen transport for both substances.

## 1 Introduction

Crystals with proton conductivity have attracted growing attention of many researchers in the last years. This is caused on the one hand by the important practical applications of these crystals in energy storage and fuel cells and on the other hand by the possibility to study the fundamental problem of the microscopic mechanism of the electric conductivity in superionic crystals [1–6]. From this point of view of particular interest are crystals with the structural peculiarity of quasi one-dimensional (1-D) chains of atomic groups bound by hydrogen bonds showing proton conductivity. Such crystals serve as very appropriate model objects in order to verify the various assumptions about the microscopic mechanisms of ionic conductivity. Our 2-D-$^2H$-NMR (nuclear magnetic resonance) exchange spectroscopy experiments [5–7] prove the presence of chemical exchange processes between deuterons of hydrogen bonds in the structure of ammonium hydrogen selenate $NH_4HSeO_4$ (AHSe), betaine phosphate (BP), betaine phosphite (BPI) and mixed crystals $BP_{1-x}BPI_x$, containing quasi 1-D chains of $SeO_4$-, $PO_4$-, or $PO_3$-tetrahedra connected by hydrogen bonds. A close relationship between chemical exchange and ionic conductivity processes was proved [7]. Potassium hydrogen selenate (KHSe) contains the quasi 1-D chains of $SeO_4$-tetrahedra connected by hydrogen bonds too and further insight into the conductivity mechanism can be expected from the study of $KHSeO_4$ crystals.

Thus, it is the aim of this paper to combine different NMR measurements with dielectric studies in order to throw light on the microscopic mechanism of ionic conductivity. In particular, a (partial) deuteration of the respective crystal samples enables the application of the powerful method of deuterium NMR for the study of proton (deuteron) transport processes. Complementary to the usual 1-D Fourier transform NMR measurements, also the 2-D chemical exchange NMR spectroscopy will be applied, because it enables one to investigate the slow deuteron exchange between well defined structural entities in the crystals and, thus, opening unique possibilities for the study of the elementary steps of these processes. It will be shown that the jump rates derived from the $^2$H-NMR exchange experiments can be directly related to the conductivity measurements.

## 2 Experimental

Deuterated (80%) potassium hydrogen selenate and partially deuterated (25%) ammonium hydrogen selenate crystals were grown from solutions with heavy water. In this process not only a deuteration of the bridging atoms but also that in the ammonium groups of AHSe were achieved. For the NMR measurements in all cases the same crystal samples were used as for dielectric investigations in order to facilitate the comparison of results.

$^2$H NMR measurements were run at a resonance frequency of 46.073 MHz on a Bruker MSL 300 NMR spectrometer. The 2-D $^2$H NMR exchange experiments were carried out by applying the echo sequence $(\pi/2)_x$-$t_1$-$(\pi/2)_{-x}$-$\tau_m$-$(\pi/2)_x$-$\tau$-$(\pi/2)_y$-$\tau$-$t_2$. The values $t_1$, $t_2$, $\tau$ and $\tau_m$ denote evolution time, acquisition time, pulse distance, and mixing time, respectively. An excitation of the complete 1-D spectrum was achieved with pulse durations of 2.5 to 4 µs. To avoid the influence of the dead time, a quadrupole spin echo sequence with a pulse distance of $\tau = 25$ µs was used. Furthermore, proton decoupling was applied to suppress the broadening of the $^2$H NMR lines due to dipolar interaction between the deuterons and the remaining protons.

Measurements of the dielectric permittivity of KHSe and AHSe crystals were perfomed at a frequency of 1 kHz with a homebuilt response analyzer. The measurements were run in the temperature range also covered by the NMR measurements. Slices with a thickness of ca. 0.8 mm were cut from the crystals and covered with a thin gold layer.

## 3 Results and Discussion

AHSe belongs to the 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 [8, 9] and the observation of protonic conductivity [1, 2]. The crystal structure of the paraelectric phase (261 to 417 K) is monoclinic (*B*2) with six formula units per unit cell [10]. The structural framework (Fig. 1a) 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*. Two types of hydrogen bonds referred to as α- and β-bonds are present in the crystal structure (Fig. 1a). In the paraelectric phase the protons in the α- bonds are disordered between two positions.

The crystal structure of the potassium hydrogen selenate $KHSeO_4$ (KHSe) is orthorhombic ($P_{bca}$) with 16 formula units per unit cell [11]. In contrast to AHSe, only one half of selenate ions are bound by hydrogen bonds in infinite chains along an *a*-glide plane of KHSe crystal (Fig. 1b). The other selenate ions are linked by a double hydrogen bridge on both sides of a symmetry center, forming an isolated dimer (Fig. 1b). The plane of the dimer is almost parallel to the

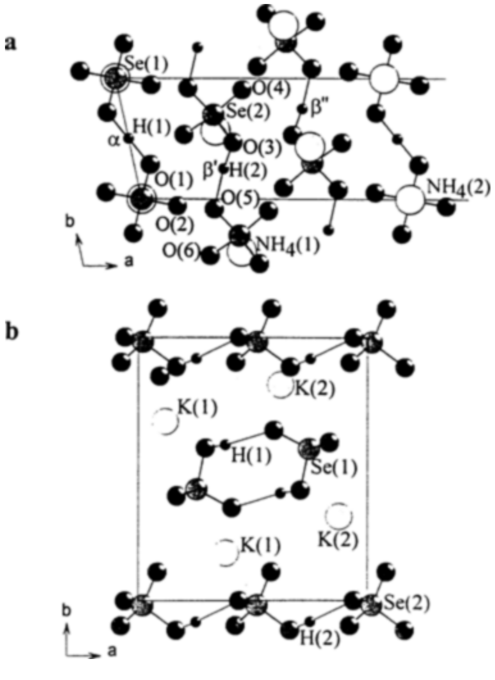

**Fig. 1.** **a** Fragment of structure of $NH_4HSeO_4$ in the paraelectric phase (half of the unit cell), **b** fragment of structure of $KHSeO_4$.

(001) crystallographic plane. Layers of quasi 1-D chains of selenate ions and dimers form the structural framework of KHSe.

Quadrupole-perturbed $^2$H NMR experiments are applied to both partially deuterated AHSe and KHSe crystals, which enable a separate characterization of the behavior of protons (deuterons) belonging to the different crystallographic positions. Typical temperature dependences of $^2$H NMR spectra in the range between room temperature and 400 K are displayed in Fig. 2 for AHSe and KHSe. The AHSe NMR spectra were acquired in the orientation where the *b*-axis is perpendicular to the external magnetic field $B_0$ and the angle between the $a^*$-axis and $B_0$-field is equal to 15°. In this orientation two line groups can be observed. The central-line doublets can be assigned to the deuterons of ammonium groups and three doublets with frequency splitting larger than 20 kHz are assigned to the deuterons in the hydrogen bonds. Our previous studies [5–7] indicated that the contribution of the ammonium group diffusion to the AHSe conductivity is negligible. Therefore, the central-line doublets will be not discussed hereinafter. The KHSe NMR spectra (Fig. 2b) were acquired in an orientation where the *b*-axis

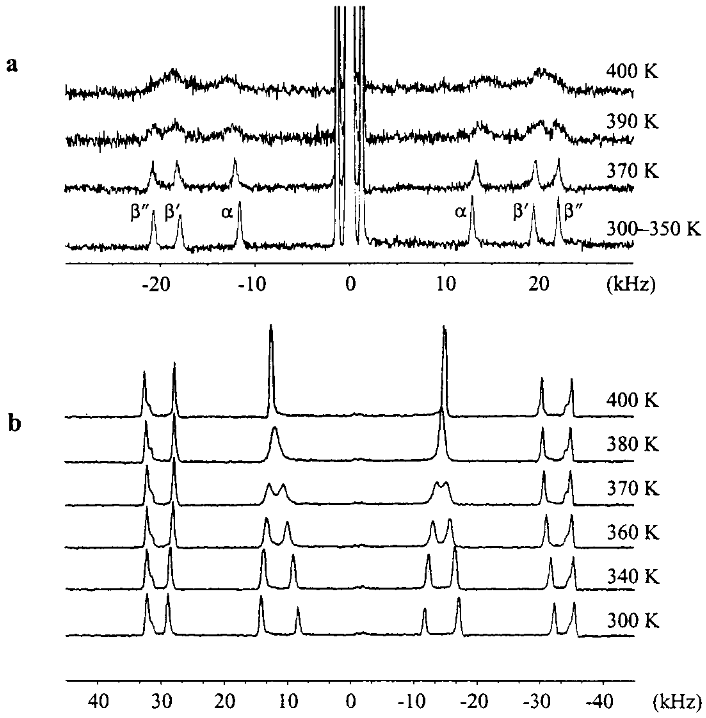

**Fig. 2.** **a** Temperature dependence of the quadrupolar line splitting in the paraelectric phase of AHSe. A crystal orientation was chosen where the *b*-axis is perpendicular to $B_0$ and the angle between the $a^*$-axis and $B_0$-field is 15°. **b** Temperature dependence of the quadrupolar line splitting of KHSe. A crystal orientation was chosen where the *b*-axis is perpendicular to $B_0$ and the angle between the *a*-axis and $B_0$-field is 40°.

is perpendicular to the external magnetic field $B_0$ and the angle between the *a*-axis and $B_0$-field is 40°. In this orientation eight lines can be observed. The two central doublets can be assigned to the deuterons in the chains of hydrogen bonds of KHSe and two doublets with frequency splitting of approximately 60 kHz are assigned to the deuterons of dimers.

One can see from Fig. 2a that at temperatures from 300 to 350 K no changes in the line shape of AHSe NMR spectra are observed. Above 350 K, a broadening of those lines can be observed which are assigned to the α- and two magnetically nonequivalent β′- and β″-positions in the hydrogen bonds (Fig. 2a). This behavior points towards the presence of chemical exchange processes but the exchange rate does not exceed the value of the quadrupolar splittings until the phase transition temperature to the superionic phase (417 K). For this reason, 1-D $^2$H-NMR experiments are not suitable for the study of details of the chemical exchange processes. It is only possible to estimate the exchange rate by means of the well-known Anderson theory (see, e.g., ref. 12), according to which the exchange rate can be calculated from the line shape. The rates thus estimated are approximately $0.5 \cdot 10^3$ $s^{-1}$ at 370 K, $2 \cdot 10^3$ $s^{-1}$ at 390 K, and $4 \cdot 10^3$ $s^{-1}$ at 400 K.

From the temperature-dependent measurements of KHSe crystal (Fig. 2b) it follows that no change in the line shape is observed at temperatures from 300 to 340 K. Above 340 K, a change only of those lines can be observed which are assigned to the deuteron positions in the quasi 1-D chains of hydrogen bonds (Fig. 2b). Above 380 K, a single doublet with splitting close to 30 kHz appears instead of the quartet NMR lines observed at room temperature from the deuterons in the chains of hydrogen bonds. The intensities of these NMR lines increase with increasing temperature. This result points towards the presence of chemical exchange processes in KHSe crystal. The exchange rates estimated by means of the Anderson theory are $1.4 \cdot 10^3$ $s^{-1}$ at 365 K, $2.8 \cdot 10^3$ $s^{-1}$ at 375 K, and $4.5 \cdot 10^3$ $s^{-1}$ at 380 K.

In order to investigate the exchange processes in the case of low exchange rates, i.e., when the exchange rate is much less than the quadrupolar splitting, the 2-D $^2$H NMR exchange spectroscopy was used for both AHSe and KHSe crystals. Details about the 2-D $^2$H NMR measurements on AHSe samples are treated in our previous work [5]. We shall only emphasize here the essential results. For AHSe, the 2-D $^2$H NMR exchange experiments were performed in the temperature range between 300 and 350 K. A typical 2-D $^2$H exchange NMR spectrum of AHSe (at 350 K with a mixing time of 3 ms) is represented in Fig. 3a. It was measured in the same orientation as the spectrum shown in Fig. 2a. The off-diagonal peaks (cf., e.g., refs. 13 and 14) in Fig. 3a indicate exchange processes between deuterons of the two types of hydrogen bonds in the structure (α- and β-bonds) and between magnetically nonequivalent positions of neighboring β-chains. The analysis shows that the exchange rates for these two processes are approximately equal. Over whole temperature interval of the paraelectric phase an exchange between the deuterons in the $ND_4$ groups and hydrogen bonds can clearly be excluded according to our results from the 2-D spec-

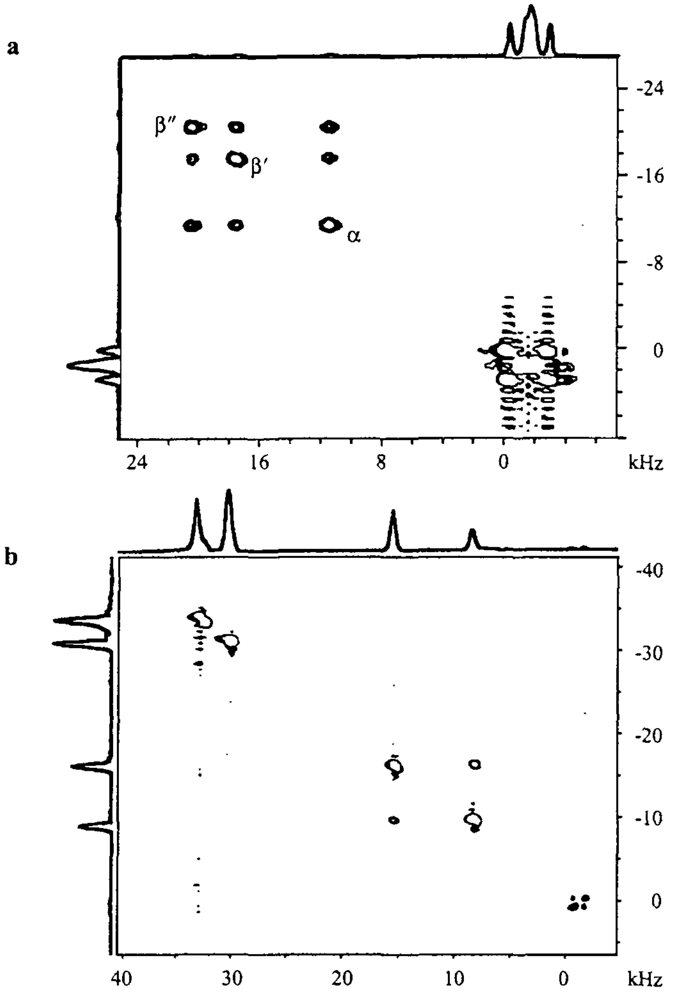

**Fig. 3.** **a** 2-D $^2$H NMR exchange spectrum for AHSe (only the upper left-hand quadrant is shown) at 350 K with a mixing time of 3 ms. The crystal orientation was as for Fig. 2a. **b** 2-D $^2$H NMR exchange spectrum for KHSe (only the upper left-hand quadrant is shown) at 300 K with a mixing time of 100 ms. The crystal orientation was as for Fig. 2b.

troscopy. For KHSe, the 2-D $^2$H NMR exchange experiments were performed in the temperature range between 300 and 340 K. A 2-D $^2$H exchange NMR spectrum of KHSe (at 300 K with a mixing time of 100 ms) is represented in Fig. 3b. It was measured in the same orientation as the spectrum shown in Fig. 2b. This 2-D spectrum also exhibits cross peaks for the magnetically nonequivalent deuteron positions in the chains of hydrogen bonds. As can be seen from Fig. 3b, up to 340 K an exchange between the deuterons in the dimer groups and chains of hydrogen bonds is not observed.

Figure 4 shows the plot of exchange rates obtained from 1-D and 2-D NMR experiments versus the reciprocal temperature for AHSe (curve 2) and KHSe (curve 1) crystals. The rates $P$ can be fitted to an Arrhenius equation with the activation energy $E_a$:

$$P(T) = p_0\exp(E_a/RT). \qquad (1)$$

It should be noted that for both crystals the data from 2-D NMR spectroscopy and the estimations from 1-D NMR spectra are consistent with each other and provide values for the activation energy of about 81 kJ/mol and a pre-exponential factor $p_0$ of $1.9 \cdot 10^{14}$ $s^{-1}$ in AHSe and $E_a = 85$ kJ/mol, $p_0 = 2.7 \cdot 10^{15}$ $s^{-1}$ in KHSe, respectively. One can see from the temperature-dependent measurements (Fig. 4, curves 1 and 2) that the rates of the exchange between deuterons of hydrogen-bound chains in both AHSe and KHSe crystals are approximately the same. This circumstance proves the existence of a similar mechanism of proton mobility in both crystals. As it was mentioned above, the layers of quasi 1-D chains of selenate ions, which are separated by layers of dimers, form the structural framework of KHSe in contrast with structural framework of AHSe. Therefore one can expect an anisotropy of conductivity in the KHSe crystals.

By means of dielectric measurements [7] the dc-conductivity ($\sigma_{dc}$) of AHSe parallel and perpendicular to the crystallographic *b*-axis (chain direction) was determined and represented in form of the plot of $\sigma_{dc} \cdot T$ versus $1/T$ (Fig. 5, curve 1). We have not found any anisotropy of $\sigma_{dc}$ in the AHSe crystals in the temperature range of 300–350 K within the limits of experimental error. The activation energies calculated from the temperature dependence of $\sigma_{dc}$ (Fig. 5, curve 1, averaged values of $E_a = 84$ kJ/mol, $\sigma_0 = 4 \cdot 10^{10}$ K/Wm) are in good agreement with that calculated from Arrhenius plots of our NMR data (Fig. 4, curve 2, $E_a = 81$ kJ/mol). In order to check whether an anisotropy of conductivity ap-

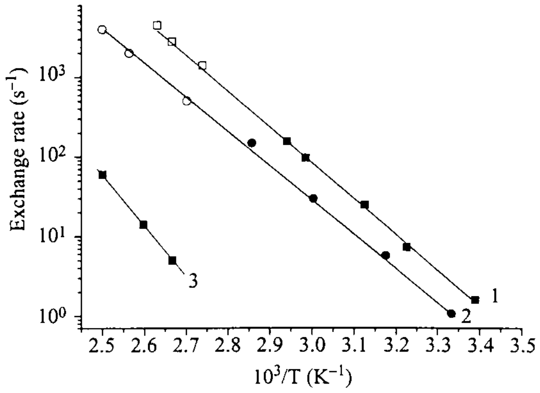

**Fig. 4.** Exchange rate between hydrogen bond deuterons of KHSe (curves 1, 3) and AHSe (curve 2) versus the reciprocal temperature. Open squares, 1-D NMR data, $KHSeO_4$; solid squares, 2-D NMR data, $KHSeO_4$; open circles, 1-D NMR data, $NH_4HSeO_4$; solid circles, 2-D NMR data, $NH_4HSeO_4$.

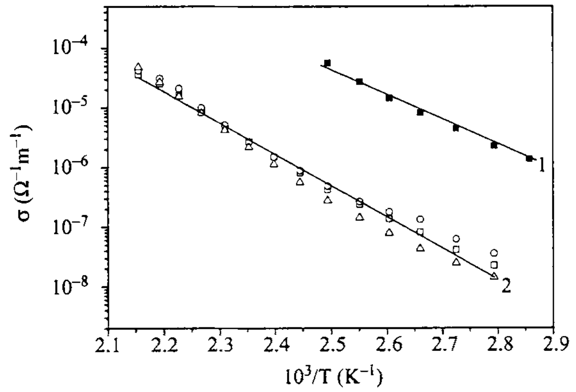

**Fig. 5.** Dc-conductivity for AHSe (curve 1) and KHSe (curve 2) versus reciprocal temperature. Open squares, $\sigma_a$; open circles, $\sigma_b$; open triangles, $\sigma_c$; $KHSeO_4$. Solid squares, $NH_4HSeO_4$.

pears in the KHSe crystals, the dc-conductivity ($\sigma_{dc}$) was determined along to the crystallographic *a*-, *b*- and *c*-axis (Fig. 5, curve 2). We have not found any anisotropy of $\sigma_{dc}$ in the KHSe crystals over the whole temperature interval within the limits of experimental error. The fit over the whole temperature interval led to the average value for the activation energy of the quantity $\sigma_{dc} \cdot T$ of $E_A = 110$ kJ/mol. The discrepancy in this activation energy, compared to the one for the exchange processes of $E_A = 85$ kJ/mol, is far beyond the experimental error. Moreover, the absolute values of the dc-conductivity in KHSe crystals were found to be more than two orders of magnitude smaller than those in AHSe crystals. Hence, in contrast to AHSe, the charge transport in KHSe did not occur by jumps of the deuterons between the neighboring chains of hydrogen bonds only.

For a better understanding of the underlying mechanism of this transport process, let us consider the structural characteristics of AHSe crystal. The minimum distance between deuterons in equivalent positions is equal to the parameter *b* of the unit cell (0.461 nm). This distance is larger than the minimum distance (0.391 nm) between the positions of deuterons in α- and β-hydrogen bonds (Fig. 1). The shortest distance between the oxygen atoms $O_1$-$O_2$ which belong to the neighborhood $SeO_4$ tetrahedra and which are not coupled by hydrogen bonds, is about 0.33 nm. There are additionally free positions for deuterons, e.g., those at the $O_3$-$O_4$ oxygen atoms separated by a very short distance (0.318 nm). This distance can be even shorter because of thermal vibrations of the $SeO_4$ tetrahedra. Due to this fact, long hydrogen bonds with short lifetimes may arise between these atoms. These considerations together with 2-D NMR data and the absence of any $\sigma_{dc}$ anisotropy allow us to conclude, that the basic mechanism of charge transport rather consists in jumps of the deuterons (protons) between the neighboring chains of hydrogen bonds. The 2-D-$^2$H-NMR measurements clearly indicate the existence of chemical exchange processes between the respective positions. Although we cannot directly observe an exchange between magnetically equivalent positions by the NMR method, the comparison of 2-D-exchange NMR results with the dielectric spectroscopy data suggests that the rates of such an exchange process are much lower than the rates of deuteron exchange between the adjacent chains of hydrogen bonds.

The distance between the neighborhood chains of hydrogen bonds in KHSe is approximately the same as those in AHSe crystals. Due to the presence of layers of dimer groups, the shortest distance between the oxygen atoms, which are not coupled by hydrogen bonds, is larger than that in AHSe. Nevertheless, this fact cannot explain the large difference of proton conductivities in KHSe and AHSe crystals.

To throw light on the microscopic mechanism of proton transport in KHSe, the 2-D $^2$H NMR exchange experiments were performed in the temperature range between 375 and 400 K. A typical 2-D $^2$H NMR spectrum of KHSe (at 400 K with a mixing time of 20 ms) is represented in Fig. 6 by the upper left-hand quadrant. It was measured in the same orientation as the 2-D spectrum shown in Fig. 3b. The off-diagonal peaks in Fig. 6 indicate exchange processes between deuterons of chains of hydrogen bonds and dimer groups in the KHSe structure and between magnetically nonequivalent positions of deuterons of dimer groups. It is well known that for both direct and indirect deuteron jumps exchange peaks may occur in the 2-D spectra, but the mixing-time dependence of the intensities of peaks originating from direct or indirect exchange exhibits different slopes of the curves. The analysis shows that the exchange rates for indirect exchange process between magnetically nonequivalent positions of deuterons of dimer groups are approximately equal to zero over the whole tem-

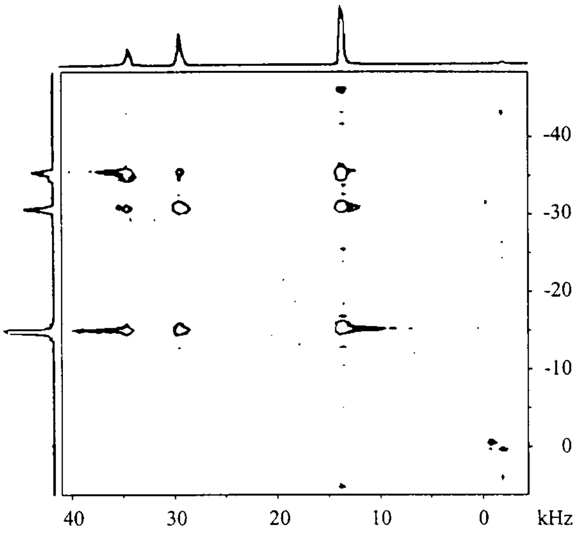

Fig. 6. 2-D $^2$H NMR exchange spectrum for KHSe (only the upper left-hand quadrant is shown) at 400 K with a mixing time of 20 ms. Crystal orientation was as for Fig. 2b.

perature range. Figure 4 (curve 3) shows the plot of exchange rates obtained from 2-D NMR experiments versus the reciprocal temperature for direct exchange processes between deuterons of chains of hydrogen bonds and dimer groups. The rate of this process was found to be more than two orders of magnitude smaller than rate of exchange process for the deuteron positions in the chains of hydrogen bonds in KHSe crystals. The data from 2-D NMR spectroscopy provide a value for the activation energy of this process of about 120 kJ/mol. Thus, the activation energies calculated from Arrhenius plots of our NMR data (Fig. 4, curve 3) and of the temperature dependence of $\sigma_{dc}$ (Fig. 5, curve 2) are in good agreement. These circumstances allow us to conclude that jumps of the deuterons (protons) between the layers of chains of hydrogen bonds and dimer groups are the necessary condition for the realization of charge transport and that the activation energy of this process is a limiting factor of the proton conductivity in $KHSeO_4$.

## Acknowledgements

We acknowledge financial support of the Russian Federation President grant "Scientific school", N.Sh.939.2003.2 and OFNRAN project 9.1.

### References

1. Blinc R., Dolinsek J., Lahajnar G., Zupancic I., Shuvalov L.A., Baranov A.I.: Phys. Status Solidi B **83**, 123 (1984)
2. Baranov A.I., Fedosyuk R.M., Schagina N.M., Shuvalov L.A.: Ferroelectrics Lett. **2**, 25 (1984)
3. Hutton S.L., Fehst I., Böhmer R., Braune M., Mertz B., Lunkenheimer P., Loidl A.: Phys. Rev. Lett. **66**, 1990–1993 (1991)
4. Ries H., Böhmer R., Fehst I., Loidl A.: Z. Phys. B **99**, 401 (1996)
5. Ivanov Yu.N., Totz J., Michel D., Klotzsche G., Sukhovsky A.A., Aleksandrova I.P.: J. Phys. Condens. Matter **11**, 3151 (1999)
6. Ivanov Yu.N., Sukhovsky A.A., Aleksandrova I.P., Totz J., Michel D.: Fiz. Tverd. Tela (St. Petersburg) **44**, 1032 (2002)
7. Totz J., Michel D., Ivanov Yu.N., Aleksandrova I.P., Petersson J., Klöpperpieper A.: Appl. Magn. Reson. **17**, 243 (1999)
8. Aleksandrova I.P., Rozanov O.V., Sukhovskii A.A., Moskvich Yu.N.: Phys. Lett. A **95**, 339 (1983)
9. Aleksandrova I.P., Colomban Ph., Denoyer F., Le Calve N., Novak A., Pasquier B., Rozicki A.: Phys. Status Solidi A **114**, 531 (1989)
10. Aleksandrov K.S., Kruglik A.I., Misyul S.V., Simonov M.A.: Kristallografiya **25**, 1142 (1980)
11. Baran J., Lis T.: Acta Crystallogr. C **42**, 270 (1986)
12. Abragam A.: Principles of Nuclear Magnetism. Oxford: Oxford University Press 1961.
13. Schmidt C., Blümich B., Spiess H.W.: J. Magn. Reson. **79**, 269 (1988)
14. Kaufmann S., Wefing S., Schaefer D., Spiess H.W.: J. Chem. Phys. **93**, 197 (1990)

**Authors' address:** Yuri N. Ivanov, L.V. Kirensky Institute of Physics, Russian Academy of Sciences, 660036 Krasnoyarsk, Russian Federation