

SEMICONDUCTORS  
AND DIELECTRICS

## Nuclear Spin Resonance Study of the Ion Mobility in a KHSeO<sub>4</sub> Crystal

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**Abstract**—The ion mobility in a crystal of partially deuterated potassium hydroselenate (KHSe) was studied using nuclear spin resonance (NSR) of <sup>1</sup>H, <sup>2</sup>H, <sup>77</sup>Se, and <sup>39</sup>K in a wide temperature range. The temperature dependences of the deuterium NSR spectra above 360 K exhibit changes in the line shape characteristic of chemical exchange processes. These exchange processes were studied in detail using two-dimensional <sup>2</sup>H NSR spectroscopy. It was ascertained that the exchange between deuterons of hydrogen bonds take place in the entire temperature range under study. However, the measured conductivity was approximately one-hundredfold lower than that estimated from the exchange frequencies. It was assumed that the low conductivity in the temperature range under study is caused by closed dimers of SeO<sub>4</sub> groups in the KHSe structure. © 2004 MAIK “Nauka/Interperiodica”.

### 1. INTRODUCTION

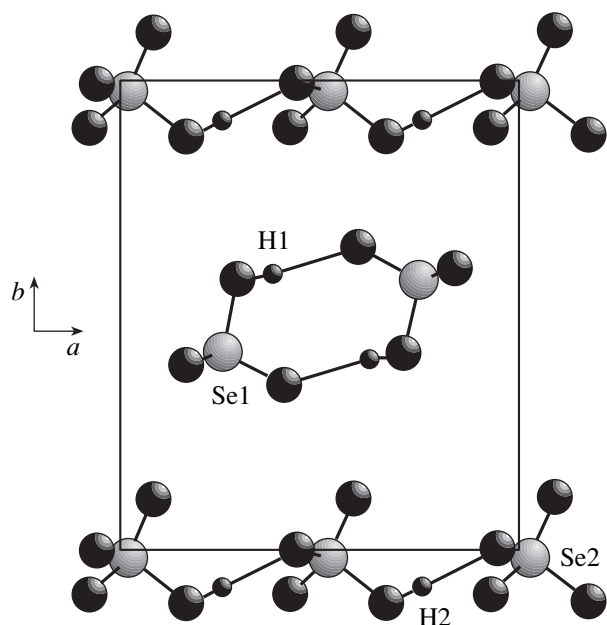
Study of the ion (chemical) exchange processes in crystals with ionic conductivity is a topical problem of solid-state physics due to the wide practical application of such compounds in modern engineering. Recently [1–3], we studied the microscopic mechanism of proton transport in the ammonium hydroselenate (AHSe) crystal. In the structure of this crystal, tetrahedral SeO<sub>4</sub> groups are joined by linear hydrogen bonds into quasi-one-dimensional chains aligned along the **b** axis. Such crystals can be good model objects to test various assumptions on microscopic mechanisms of ionic conductivity. In [1–3], it was shown that the ionic conductivity in AHSe and its isotropic nature are caused by proton exchanges between hydrogen bond chains. It might be expected that proton exchange similar to that in the AHSe paraelectric phase also takes place in other crystals with hydrogen bond chains. From this viewpoint, it is of interest to study ion transport in the potassium hydroselenate (KHSe) crystal, whose structure is characterized by hydrogen bond chains that alternate with layers of closed “dimers” of SeO<sub>4</sub> groups [4].

As in the case of the AHSe crystal, KHSe was partially deuterated (~80% of protons are substituted by deuterium nuclei), which allowed us to apply NSR of quadrupole nuclei to study proton (deuteron) transport processes. In addition to conventional NSR Fourier spectroscopy, we used two-dimensional (2D) NSR spectroscopy, which provided a unique opportunity to study elementary processes in the chemical exchange of deuterons. Since, apart from protons, other lattice ions can contribute to the conductivity, NSR spectra of

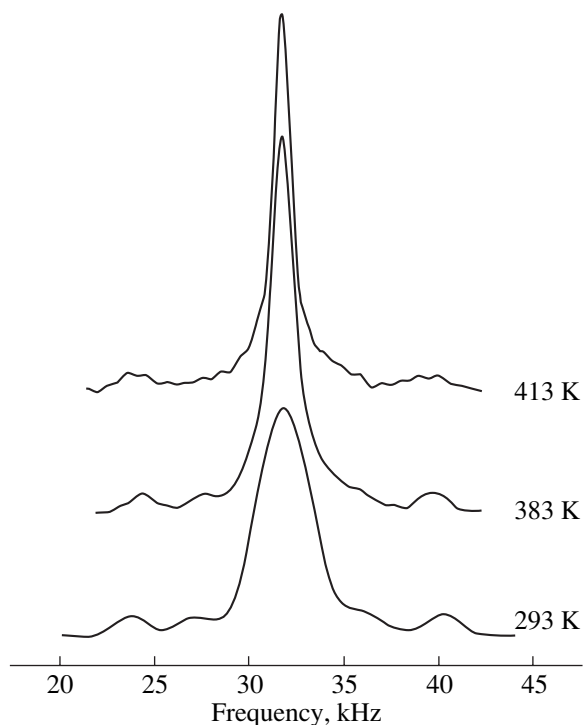
<sup>39</sup>K and <sup>77</sup>Se were studied in a wide temperature range. The NSR spectroscopy data were compared to dielectric measurements at a frequency of 1 kHz.

### 2. EXPERIMENTAL

Partially deuterated (80%) KHSeO<sub>4</sub> crystals were grown from an aqueous solution containing excess H<sub>2</sub>SeO<sub>4</sub> and an appropriate amount of heavy water. The same samples were used in NSR and dielectric measurements. <sup>2</sup>H NSR measurements were carried out using a BRUKER MSL 300 spectrometer with a Larmor frequency of 46.073 MHz. The duration of a 90° pulse was ~4 μs. To eliminate the “dead time” effect of the NSR spectrometer receiver, a spin-echo sequence with a time of 25 μs between pulses was used. Moreover, proton decoupling was employed to suppress broadening of <sup>2</sup>H NSR lines because of the dipole-dipole interaction with remaining protons. Two-dimensional NSR studies were carried out using a spin-echo sequence  $(\pi/2)_x - t_1 - (\pi/2)_{-x} - \tau_m - (\pi/2)_x - \tau - (\pi/2)_y - \tau - t_2$ , where  $t_1$ ,  $t_2$ ,  $\tau$ , and  $\tau_m$  are the evolution time, measurement time, time between pulses, and mixing time, respectively. NSR spectra of <sup>39</sup>K and <sup>77</sup>Se were measured using an AVANCE 300 spectrometer at Larmor frequencies of 13.9 and 57.301 MHz, respectively. To increase the signal intensity from rare <sup>77</sup>Se nuclei, the cross-polarization method [5] was used. <sup>1</sup>H NSR measurements were performed using a laboratory-made pulsed NSR spectrometer with a proton Larmor frequency of 27.0 MHz.



**Fig. 1.** Fragment of the  $\text{KHSeO}_4$  structure (hydrogen bond chains and one chain of dimers).



**Fig. 2.** Temperature dependence of proton spectra in  $\text{KHSe}$ .

The dielectric susceptibility was measured at a frequency of 1 kHz using the bridge method in the temperature range 350–450 K. Samples ~0.8-mm thick were cut from a  $\text{KHSe}$  single crystal. Thin gold films were employed as electrodes in dielectric measurements.

### 3. RESULTS AND DISCUSSION

The  $\text{KHSe}$  crystal is characterized by orthorhombic symmetry; its space group is  $P_{bcac}$ ,  $a = 8.690$  Å,  $b = 10.053$  Å, and  $c = 19.47$  Å ( $Z = 16$ ) [4]. The main difference between the  $\text{KHSe}$  structure and the previously studied  $\text{AHSe}$  structure [6] is that only half the  $\text{SeO}_4$  groups in  $\text{KHSe}$  are hydrogen-bonded into infinite chains similar to those in the  $\text{AHSe}$  structure and aligned along the  $a$  axis. The remaining  $\text{SeO}_4$  groups are hydrogen-bonded in pairs into relatively separate dimers (Fig. 1). Each dimer is characterized by a symmetry center, and the dimer plane is almost parallel to the (001) crystallographic plane. The positions of hydrogen bond protons were not determined in [4]; however, they can be approximately determined from structural data on the potassium hydrosulfate  $\text{KHSO}_4$  crystal [7, 8] by taking into account that these crystals are isomorphous. However, this assumption is not quite correct, since it is indicated in [4] (based on data on the relevant  $\text{O}\cdots\text{O}$  distances) that hydrogen bonds in the  $\text{KHSe}$  crystal are significantly stronger than those in  $\text{KHSO}_4$ .

As mentioned above, ~80% of protons in the  $\text{KHSe}$  crystal are substituted by deuterium nuclei; i.e., protons are “rare” nuclei. This circumstance allows precise localization of protons in  $\text{KHSe}$  using  $^1\text{H}$  NSR. Figure 2 shows typical  $^1\text{H}$  NSR spectra in  $\text{KHSe}$  measured at various temperatures and for a crystal orientation such that the  $c$  axis is perpendicular to the external magnetic field  $\mathbf{B}_0$  and the angle between the  $a$  axis and the field  $\mathbf{B}_0$  is  $45^\circ$ . We can see from Fig. 2 that two Pake doublets belonging to two magnetically nonequivalent pairs of dimer protons are well resolved due to a significant decrease in the intermolecular dipole–dipole interaction between protons. The central spectral line belongs to protons of hydrogen bond chains and dimers in which only one proton is substituted by deuterium. It is worth mentioning that the degree of sample deuteration can be determined independently from the relative intensity of spectral components. The intensity of each component of the Pake doublets is  $4.7 \pm 0.3\%$  of the total intensity of the proton spectrum. Simple calculations show that this value corresponds to substitution of 81.2% of protons by deuterium. The orientation dependences of doublet splitting were used to determine the distances between dimer protons and the proton–proton vector orientation in the crystal ( $r = 2.450$  Å; direction cosines, 0.590,  $-0.810$ ,  $-0.091$ ). Since the determined parameters differ substantially from the values obtained for the  $\text{KHSO}_4$  structure ( $r = 2.7197$  Å; direction cosines, 0.7485,  $-0.6630$ ,  $-0.0139$ ) [7], the orientation dependences of the second moments of the proton spectrum with respect to the three crystallographic axes were measured to correct the coordinates of all protons in  $\text{KHSe}$ . Figure 3a shows the experimental (symbols) and calculated (solid lines) angular dependences of the second moments of the  $^1\text{H}$  NSR spectra. The second moments were calculated using the proton coordinates

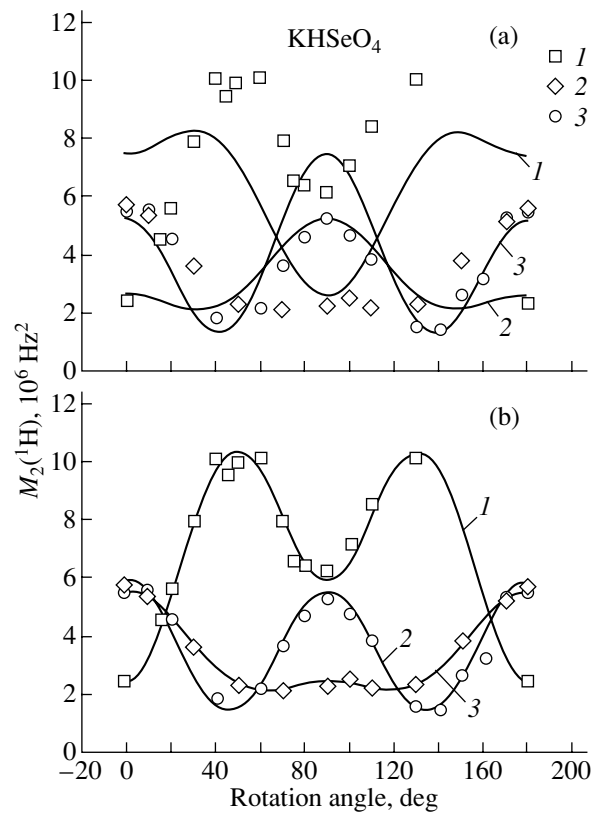
determined for the  $\text{KHSO}_4$  structure and taking into account all magnetic isotopes of the sample in a sphere 40 Å in radius. We can see from Fig. 3b that the experimental and calculated angular dependences of the second moments of the proton spectra largely disagree. We developed a computer program allowing determination of the proton positions in the structure by varying the proton coordinates, which provides the best fit to the experimental curves. The determined proton coordinates are listed in Table 1. The angular dependences of the second moments of the proton spectra calculated using the data from Table 1 are shown in Fig. 3b, together with the experimental data. The corrected proton coordinates are also in good agreement with the results of the Pake analysis of the proton spectra.

The temperature dependences of proton spectra of KHSe were studied in the temperature range 283–403 K. Figure 2 shows  $^1\text{H}$  spectra of KHSe at temperatures of 283, 383, and 413 K. We can see from Fig. 2 that the splittings between the components of Pake doublets remain unchanged in the entire temperature range under consideration, while the width of the spectral components gradually decreases with increasing temperature. These data indicate that the protons belonging to hydrogen bond chains are mobile and that there is not an appreciable exchange of dimer protons. Of course, it is impossible to determine the proton motion characteristics from these spectra. We can make only estimates (see [9, Section 10]) of the correlation time  $\tau_c$  of proton exchange in hydrogen bond chains by using the change in the spectral component width. The estimations yield  $\tau_c \sim 5 \times 10^{-4}$  s at  $T = 383$  K.

To study the microscopic characteristics of KHSe, we recorded  $^2\text{H}$  NSR spectra of partially deuterated KHSe. Deuterium nuclei have an electric quadrupole moment, which allows determination of the electric field gradient (EFG) tensor at the position of the nucleus under study. In the case of a strong external magnetic field  $\mathbf{B}_0$ , when the Zeeman interaction energy significantly exceeds the interaction energy between the nucleus quadrupole moment and the intracrystalline field. The latter interaction results in perturbation of the equidistant Zeeman levels and in splitting of the NSR line into  $2I$  components ( $I$  is the nucleus spin) arranged symmetrically with respect to the frequency  $\nu_0$  of the Larmor precession in the field  $\mathbf{B}_0$  [10]. Hence, the deuteron NSR spectrum ( $I_D = 1$ ) consists of doublets, whose number for a single-crystal sample is dictated in general by the number of magnetically nonequivalent deuterium nuclei. The quadrupole splitting  $\nu_2 - \nu_1$  is given by [10]

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

where  $Q$  is the quadrupole moment of the nucleus,  $e$  is the electron charge,  $h$  is Planck's constant, and  $V_{zz}$  is the  $z$  component of the EFG at the nucleus site (field  $\mathbf{B}_0$  is directed along the  $z$  axis). The orientation dependences



**Fig. 3.** Calculated (solid curves) and experimental (symbols) angular dependences of the second moments of proton spectra in KHSe for rotation about the **a**, **b**, **c** axes (curves 3, 2, 1, respectively). The proton coordinates (a) are taken from [7] and (b) determined by fitting.

of quadrupole splittings can be used to determine (using the well-known Volkoff method [11]) all components  $V_{ij}$  of the EFG tensor for each structurally nonequivalent position of deuterium in the crystal in the laboratory coordinate system. The EFG tensor (instead of  $V_{ij}$ , for simplicity, we use their values  $\Phi_{ij}$  in frequency units) is a symmetric second-rank tensor with zero trace and reflects the point symmetry of the position of the nucleus under study.

It is known that the direction of the principal axis of the EFG tensor  $\Phi_{33}$  for hydrogen bonds approximately coincides with the O...O bond direction [12], which makes it possible to attribute each EFG tensor to a certain hydrogen bond in the crystal. Thus, the  $^2\text{H}$  magnetic resonance in partially deuterated KHSe extends

**Table 1.** Corrected proton coordinates (in units of the unit cell parameters) in the KHSe crystal determined from the angular dependences of the second moments

	$x$	$y$	$z$
H1	0.4179	0.6025	0.0061
H2	0.2278	0.0907	0.2862

**Table 2.** Parameters of EFG tensors at  $T = 295$  K for protons of hydrogen bond chains H2 and of dimers H1 of the KHSe crystal

H2				H1			
Principal values of EFG tensors $\Phi_{ii}$ , kHz	Direction cosines with respect to the crystallographic axes			Principal values of EFG tensors $\Phi_{ii}$ , kHz	Direction cosines with respect to the crystallographic axes		
	a	b	c		a	b	c
$\Phi_{11} = -125.0$	0.164	-0.342	0.926	$\Phi_{11} = -142.6$	-0.016	0.046	0.999
$\Phi_{22} = -95.4$	-0.459	0.805	0.377	$\Phi_{22} = -103.6$	-0.186	0.981	-0.48
$\Phi_{33} = 219.4$	-0.874	-0.485	-0.027	$\Phi_{33} = 244.7$	-0.982	-0.187	0.0

the capabilities of the NSR method significantly and makes it possible to separately study the dynamic characteristics of protons belonging to hydrogen bonds of chains and dimers.

Two different EFG tensors were determined from the angular dependences of the  $^2\text{H}$  NSR spectra at 300 K (Table 2). The principal axes ( $\Phi_{33}$ ) of these two tensors almost coincide in direction with the hydrogen bonds of O...O chains and dimers, respectively. Thus, it is possible to unambiguously relate each of these EFG tensors to the corresponding proton position in the KHSe crystal structure.

The typical temperature dependence (in the range from 295 to 400 K) of  $^2\text{H}$  NSR spectra in KHSe is shown in Fig. 4. These spectra were measured for the crystal orientation where the **b** axis is perpendicular to the external magnetic field  $\mathbf{B}_0$  and the angle between the **a** axis and the field  $\mathbf{B}_0$  is  $40^\circ$ . In this case, two quartets of lines are observed. The two central doublets (Fig. 4) correspond to deuterons of hydrogen bond

chains, and the two doublets with splitting  $\sim 60$  kHz belong to dimer deuterons. It follows from Fig. 4 that there are no significant changes in the spectrum of dimer deuterons in the entire temperature range under study. In the spectra of hydrogen bond deuterons, appreciable changes take place at temperatures above 350 K. The lines of the inner quartet initially broaden with temperature and form a doublet above 375 K. Its components narrow as the sample is further heated. These data unambiguously indicate that there is a chemical exchange of deuterons in the system of hydrogen bonds of the crystal. The chemical exchange rate can be estimated from the temperature dependence of the spectra by using the NSR line shape and the well-known Anderson theory [13]. The chemical exchange rates obtained in this way are  $1.4 \times 10^3$ ,  $2.8 \times 10^3$ , and  $4.5 \times 10^3$  s $^{-1}$  at 365, 375, and 380 K, respectively.

To obtain more detailed information on the microscopic mechanism of deuteron mobility, the exchange rate, and the activation energy for this process, the 2D  $^2\text{H}$  NSR spectroscopy technique was used. A mathematical description of the chemical exchange processes and exchange rate calculations from 2D NSR spectra can be found in many well-known papers [14, 15] and are briefly described in our previous papers [1–3]. The chemical exchange is described by the basic equation [9]

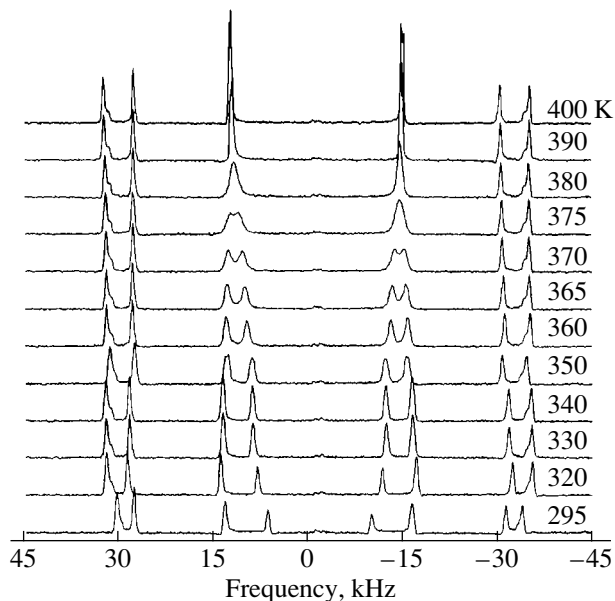
$$\frac{\partial n_i}{\partial t} = \sum_j^n p_{ij} n_j, \quad (2)$$

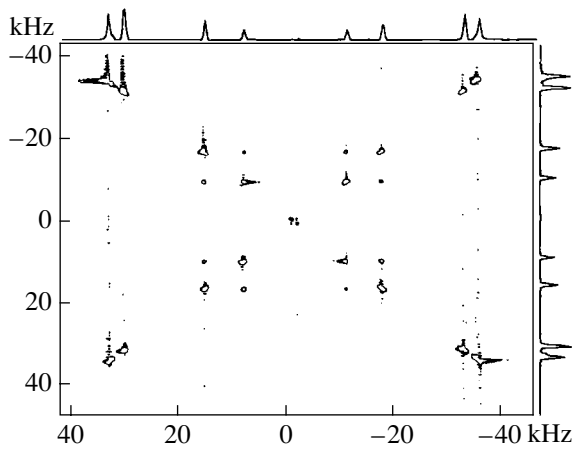
where  $p_{ij}$  is the probability of the transition between positions  $i$  and  $j$  and  $n_j$  is the population of the corresponding state.

In matrix notation, Eq. (2) can be written as  $\dot{\mathbf{n}} = \hat{p} \mathbf{n}$ , and its solution is

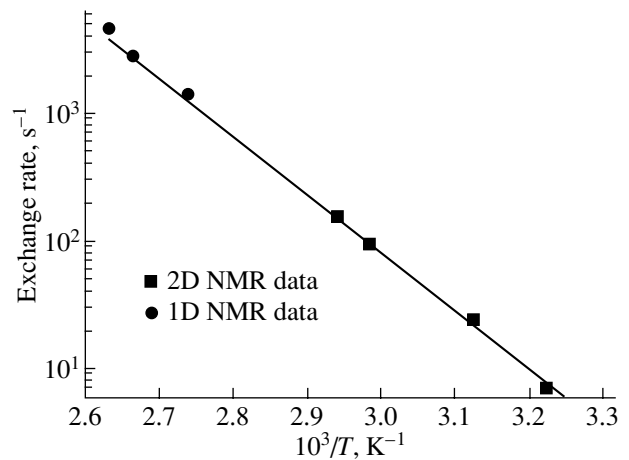
$$\mathbf{n}(t) = \exp(\hat{p} \cdot t) \mathbf{n}_0 = \hat{A}(t) \mathbf{n}_0, \quad (3)$$

where the components of the vector  $\mathbf{n}_0 = \{n_{01}, \dots, n_{0i}\}$  –  $n_{0i}$  are equal to the number of deuterons at position  $i$  at the instant of time  $t = 0$  and the components of the vector  $\mathbf{n}(t) = \{n_1, \dots, n_i\}$  –  $n_i$  are equal to the number of deuterons at the same position at the instant  $t = \tau_m$ . The components  $A_{ij}(t)$  of the exchange matrix  $\hat{A}(t)$  in Eq. (3),

**Fig. 4.** Temperature dependence of quadrupole splittings in KHSe.



**Fig. 5.** 2D <sup>2</sup>H NSR exchange spectrum of KHSe at a temperature of 300 K and a mixing time of 100 ms.



**Fig. 6.** Temperature dependence of the deuteron exchange rate in KHSe according to one- and two-dimensional NSR spectroscopy data.

which completely define the dynamics of the deuteron (proton) exchange in the crystal, can be determined from the intensities of the corresponding off-diagonal peaks of 2D NSR spectra of deuterium [14, 15]. 2D NSR experiments in KHSe were carried out in the temperature range from 300 to 340 K and in the same orientation as in the case of the one-dimensional (1D) spectra in Fig. 4. This temperature range was chosen since the mixing time  $\tau_m$  in 2D experiments should satisfy the condition  $T_2 < \tau_m < T_1$ ; moreover, the intensity of off-diagonal peaks at this mixing time should be sufficient to accurately determine the exchange rate. These conditions can be satisfied only in the indicated temperature range. The typical 2D <sup>2</sup>H NSR nuclear spectrum of KHSe (at 300 K and a mixing time of 100 ms) is shown in Fig. 5. The off-diagonal peaks (see, e.g., [14, 15]) in Fig. 5 suggest that the deuteron exchange takes place between magnetically nonequivalent positions of deuterons belonging to nearby chains of hydrogen bonds. In this case, as in AHSe, a simple two-position exchange is observed. To determine the rate of this process, a single measurement with a correctly selected mixing time at a given temperature is sufficient [1].

Figure 6 shows the temperature dependence of the exchange rate constructed using the data from 1D and 2D NSR spectroscopy. The solid line is a fit of this dependence to the Arrhenius equation with an activation energy  $E_a$ :

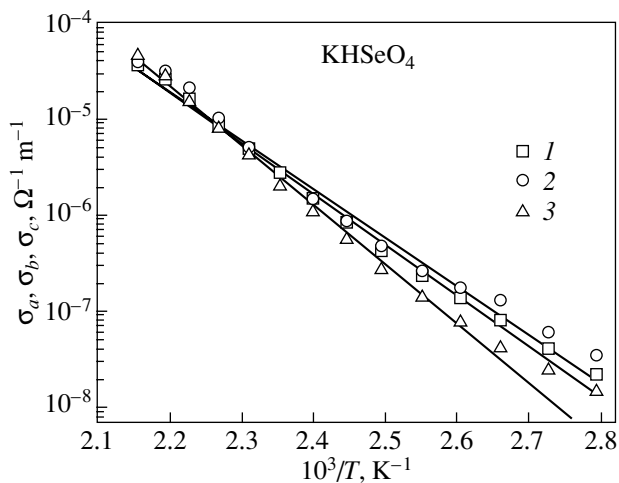
$$p(T) = p_0 \exp(E_a/RT). \tag{4}$$

It should be noted that the 2D-spectroscopy data and the estimates based on 1D spectra agree well and yield a value of  $\sim 85$  kJ/mol for the activation energy of the exchange process and the preexponential factor  $p_0 = 2.7 \times 10^{15} \text{ s}^{-1}$ . It follows from Fig. 6 that the temperature dependences of the line shape observed in the 1D spectra of deuterium at higher temperatures are dictated by the same deuteron exchange type as the cross peaks in 2D spectra.

As noted above, in contrast to the AHSe crystal, layers of hydrogen bond chains in KHSe are separated by dimer layers, and the exchange process can result in exchange only within a single layer. Hence, strong anisotropy in the ionic conductivity can be expected in KHSe. However, no appreciable anisotropy was detected in this crystal in preliminary measurements. Since, apart from protons, other ions can, in principle,

**Table 3.** Parameters of the magnetic shielding tensors at  $T = 295$  K for two structurally nonequivalent selenium nuclei of the KHSe crystal

Principal values of MS tensors $\Phi_{ii}$ , Hz	Se1			Principal values of MS tensors $\Phi_{ii}$ , Hz	Se2		
	Direction cosines with respect to the crystallographic axes				Direction cosines with respect to the crystallographic axes		
	a	b	c		a	b	c
$\Phi_{11} = -12531$	0.0	0.0	-1	$\Phi_{11} = -10171$	-0.466	0.837	-0.285
$\Phi_{22} = -842$	0.981	-0.193	0.0	$\Phi_{22} = -3138$	-0.200	0.214	0.956
$\Phi_{33} = 12045$	0.193	0.981	0.0	$\Phi_{33} = 12795$	0.862	0.503	0.068



**Fig. 7.** Temperature dependence of the KHSe crystal conductivity along the **a**, **b**, **c** crystallographic axes.

contribute to the KHSe conductivity, we studied the temperature dependences of  $^{77}\text{Se}$  and  $^{39}\text{K}$  NSR spectra.

The parameters of the two tensors of magnetic shielding (MS) at selenium nucleus sites that belong to  $\text{SeO}_4$  groups hydrogen-bonded into chains and dimers, respectively, were determined from the orientation dependence of  $^{77}\text{Se}$  NSR spectra at a temperature of 295 K (Table 3). The MS tensor parameters are typical of hydrogen-bonded  $\text{SeO}_4$  groups. The parameters of both MS tensors remain unchanged in the entire temperature range under consideration (295–420 K). Changes were likewise not detected in  $^{39}\text{K}$  NSR spectra in this range. Thus, both selenium and potassium nuclei cannot contribute appreciably to the KHSe ionic conductivity (at least up to 420 K).

Dielectric measurements were carried out at a fixed frequency of 1 kHz for three cuts in the KHSe crystal perpendicular to the **a**, **b**, **c** crystallographic axes. The bridge method with a measuring field of  $\sim 1$  V/mm was used. The measurement results are shown in Fig. 7. Significant anisotropy is not observed in the ionic conductivity, which contradicts the above considerations. Moreover, the measured conductivity is approximately two orders of magnitude lower than that estimated by us from the exchange frequencies obtained in the 2D experiments. It is also worth noting that the activation energy determined from the temperature dependence of the conductivity ( $\sim 110$  kJ/mol) differs significantly from that for the exchange process observed in NSR experiments using the deuterium 2D spectroscopy technique (85 kJ/mol).

As mentioned above, this situation differs from that observed in the AHSe crystal, where the proton

exchange between chains (approximately with the same activation energy and exchange rates) completely defines the ionic conductivity. This seems to be caused by dimers existing in the KHSe structure, which are not involved in the proton exchange in the temperature range under study.

We are currently carrying out additional studies to refine data on the proton transport mechanism in the KHSe crystal.

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#### REFERENCES

1. Yu. N. Ivanov, J. Totz, D. Michel, G. Klotzsche, A. A. Sukhovskiy, and I. P. Aleksandrova, *J. Phys.: Condens. Matter* **11** (18), 3151 (1999).
2. J. Totz, D. Michel, Yu. N. Ivanov, I. P. Aleksandrova, J. Petersson, and A. Klöpperpieper, *Appl. Magn. Reson.* **17** (2–3), 243 (1999).
3. Yu. N. Ivanov, A. A. Sukhovskiy, I. P. Aleksandrova, J. Totz, and D. Michel, *Fiz. Tverd. Tela* (St. Petersburg) **44** (6), 1032 (2002) [*Phys. Solid State* **44**, 1077 (2002)].
4. J. Baran and T. Lis, *Acta Crystallogr. C* **42** (3), 270 (1986).
5. A. Pines, M. G. Gibby, and J. S. Waugh, *J. Chem. Phys.* **59** (2), 569 (1973).
6. K. S. Aleksandrov, A. I. Kruglik, S. V. Misyul', and M. A. Simonov, *Kristallografiya* **25** (5), 1142 (1980) [*Sov. Phys. Crystallogr.* **25**, 654 (1980)].
7. F. A. Cotton, B. A. Frenz, and D. L. Hunter, *Acta Crystallogr. B* **31** (1), 302 (1975).
8. F. Payan and R. Haser, *Acta Crystallogr. B* **32** (6), 1875 (1976).
9. A. Abragam, *The Principles of Nuclear Magnetism* (Clarendon, Oxford, 1961; Inostrannaya Literatura, Moscow, 1963).
10. R. V. Pound, *Phys. Rev.* **79** (4), 685 (1950).
11. G. V. Volkoff, H. E. Petch, and D. W. Smellie, *Phys. Rev.* **84** (3), 602 (1951).
12. J. Soda and T. Chiba, *J. Phys. Soc. Jpn.* **26** (2), 249 (1969).
13. P. W. Anderson, *J. Phys. Soc. Jpn.* **9** (3), 316 (1954).
14. C. Schmidt, B. Blümich, and H. W. Spiess, *J. Magn. Reson.* **79** (2), 269 (1988).
15. S. Kaufmann, S. Wefing, D. Schaefer, and H. W. Spiess, *J. Chem. Phys.* **93** (1), 197 (1990).

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