

Micromechanism of Proton Conduction in a KHSeO_4 Crystal

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Abstract—The proton exchange in a potassium hydrogen selenate crystal is investigated in detail. Partial deuteration of the crystal (approximately 80% of the protons are replaced by deuterons) makes it possible to use the method of nuclear magnetic resonance (NMR) on quadrupole nuclei to perform research into proton (deuteron) transport. In addition to conventional Fourier-transform NMR spectroscopy, elementary processes of deuteron chemical exchange are studied by two-dimensional NMR spectroscopy, which provides unique information regarding these processes. Slow exchange between protons of hydrogen bond chains and dimers consisting of two SeO_4 groups is revealed. It is established that this process is responsible for the proton conduction in the potassium hydrogen selenate. The NMR data are compared with the results of dielectric measurements carried out at a frequency of 1 kHz.

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1. INTRODUCTION

In our recent work [1], the ion mobility in a crystal of partially deuterated potassium hydrogen selenate (PHS) was investigated by ^1H , ^2H , ^{77}Se , and ^{39}K NMR spectroscopy over a wide range of temperatures. In particular, it was established that the parameters (such as the rate and activation energy) of proton exchange in the PHS crystal and the paraelectric phase of the related ammonium hydrogen selenate (AHS) crystal studied in our earlier works [2–4] are close to each other, whereas the parameters of the macroscopic ionic conductivity in these crystals differ significantly. It can be assumed that the origin of these differences lies in the structural features of the crystals under investigation. The fundamental difference in the structures of the PHS and AHS crystals is that, in the former crystal, half of the SeO_4 groups are joined together by hydrogen bonds into infinite chains extended along the \mathbf{a} axis (similar to the infinite chains formed in the structure of the AHS crystal). The other SeO_4 groups are linked together in pairs by two hydrogen bonds into relatively isolated dimers. It was found that, in the PHS crystal, as in the paraelectric phase of the AHS crystal, the exchange between positions of deuterons in hydrogen bonds of the chains occurs in the temperature range 290–375 K, even though no exchange with the participation of dimer protons was revealed in [1]. It is significant that the measured electrical conductivity is approximately two orders of magnitude lower than the electrical conductivity estimated from the rates of the exchange. Moreover, the activation energy determined from the temperature dependence of the electrical conductivity differs

substantially from the activation energy obtained from the temperature dependence of the rate of the proton exchange. This situation differs from that observed earlier for the AHS crystal [2–4], in which the proton exchange between chains at approximately equal activation energies and close rates of the exchange at the same temperature is completely responsible for the ionic conduction. Since the layers formed by hydrogen bond chains in the PHS crystal are separated by layers composed of dimers, it is assumed that the revealed exchange process is determined only by the exchange within one layer consisting of the chains. In this case, a strong anisotropy of the ionic conductivity should be expected. However, according to our experimental results obtained in [1], no noticeable conductivity anisotropy is observed in the PHS crystal. The temperature dependences of the ^{77}Se and ^{39}K NMR spectra [1] suggest that ^{77}Se and ^{39}K ions cannot contribute significantly to the electrical conduction of the PHS crystal. In the present work, the PHS crystal was investigated by two-dimensional NMR spectroscopy over a temperature range wider than that used in our earlier work. This made it possible to reveal the exchange process that provides proton transport through a “narrow neck” and eventually determines the parameters of the macroscopic electrical conductivity in the PHS crystal.

2. SAMPLE PREPARATION AND EXPERIMENTAL TECHNIQUE

Partially deuterated (80%) KHSeO_4 crystals were grown from an aqueous solution containing an excess

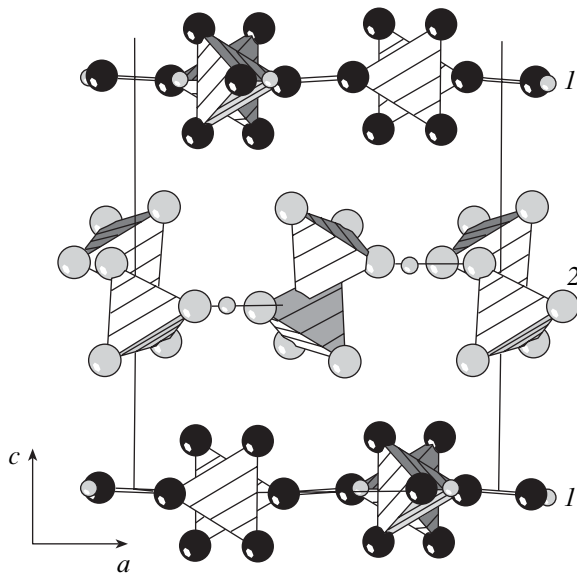


Fig. 1. A structural fragment of the KHSeO_4 crystal in the projection onto the (010) plane. Half of the unit cell is shown. The potassium atoms are omitted for clarity. The structure is formed by dimer layers 1 and chain layers 2.

of H_2SeO_4 and an appropriate amount of heavy water. The same samples were used for nuclear magnetic resonance and dielectric measurements. The ^2H NMR investigations were carried out on a BRUKER MSL 300 NMR spectrometer operating at a Larmor frequency of 46.073 MHz. The width of a 90° pulse was approximately equal to $4 \mu\text{s}$. A spin echo sequence with a time interval of $25 \mu\text{s}$ between pulses was used in order to exclude the effect of the dead time of the NMR spectrometer receiver. Moreover, proton decoupling was employed to suppress the broadening of the ^2H NMR lines due to the dipole–dipole interaction with the remaining protons. The two-dimensional NMR measurements were performed in the temperature range 375–400 K with the use of the following 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 is the evolution time, t_2 is the measurement time, τ is the time interval between pulses, and τ_m is the mixing time. Since the exchange processes under investigation involved protons of several structural types, the intensities of the cross peaks were also measured at several mixing times individually chosen for each temperature.

3. RESULTS AND DISCUSSION

The PHS crystal has orthorhombic symmetry; space group $Pbca$; and the unit cell parameters $a = 8.690 \text{ \AA}$, $b = 10.053 \text{ \AA}$, and $c = 19.47 \text{ \AA}$ ($Z = 16$) [5]. A structural fragment of the PHS crystal in the projection onto the (010) plane is depicted in Fig. 1 (one-half of the unit cell is shown, and the potassium atoms are omitted for clarity). Chains and dimers form layers in the (001)

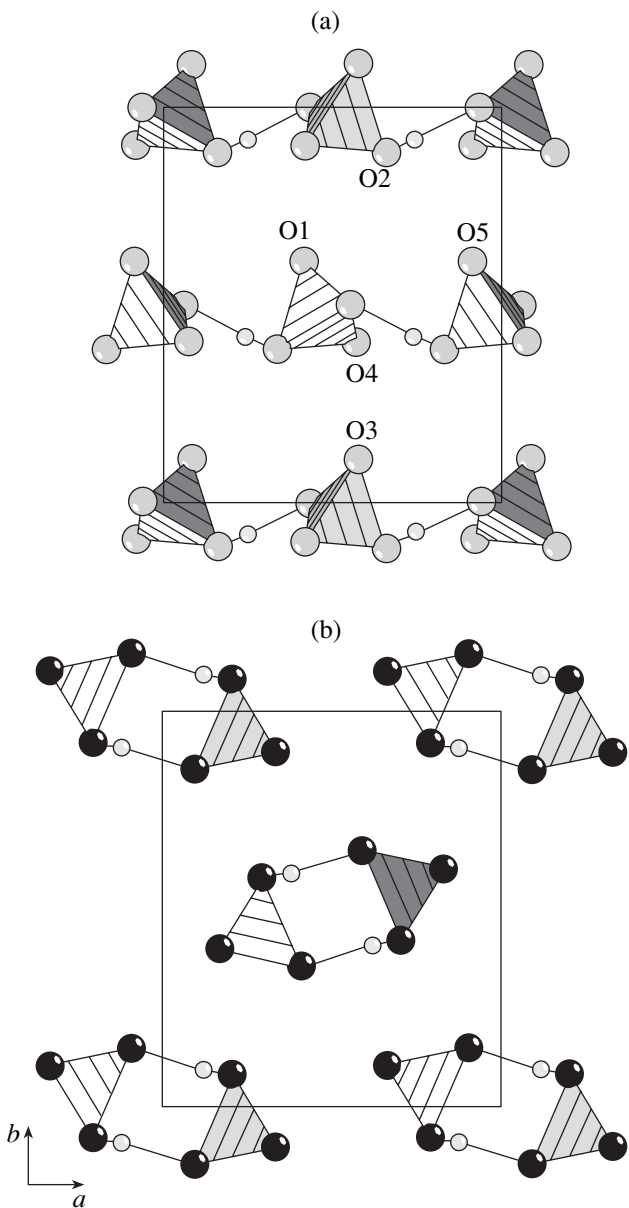


Fig. 2. Projections of (a) the layer formed by hydrogen bond chains and (b) the layer consisting of dimers onto the (001) plane. The oxygen atoms of the SeO_4 groups in the layer of chains are numbered conventionally and belong to the same structural type (O2 according to the Baran–Lis notation [5]).

plane. The layer consisting of hydrogen bond chains and the layer composed of dimers formed by the second half of the SeO_4 groups are shown in Figs. 2a and 2b, respectively. Each dimer has a center of symmetry, and the dimer plane is virtually parallel to the (001) crystallographic plane. As can be clearly seen from Fig. 1, the dimer layers separate the chain layers. The proton positions in the hydrogen bonds were refined in our earlier work [1].

As was noted earlier in [1], the temperature dependences of the ^2H NMR spectra of the KHSeO_4 crystal

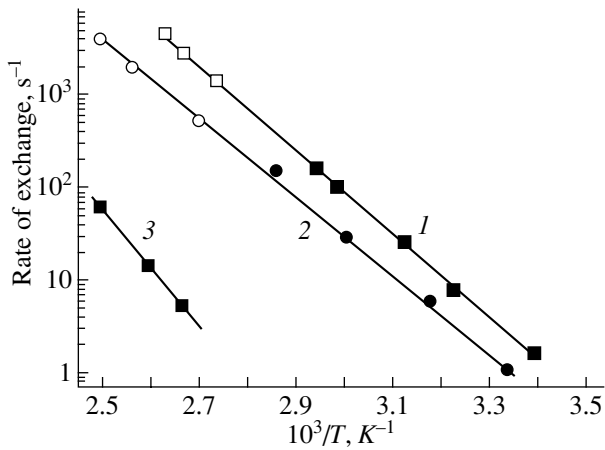


Fig. 3. Temperature dependences of the rate of deuteron exchange in hydrogen bond chains of the (1) KHSeO₄ and (2) NH₄HSeO₄ crystals and (3) the rate of direct deuteron exchange in chains and dimers of the KHSeO₄ crystal according to the one-dimensional (open symbols) and two-dimensional (closed symbols) NMR data.

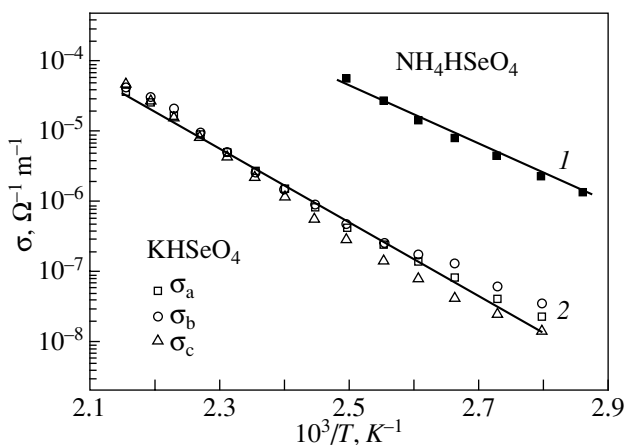


Fig. 4. Temperature dependences of the electrical conductivity of the (1) NH₄HSeO₄ and (2) KHSeO₄ crystals along the crystallographic axes **a**, **b**, and **c**.

indicate that the protons in the hydrogen bond chains are mobile, whereas the protons of dimers are not involved in the exchange processes at temperatures in the range 300–375 K. The temperature dependences of the rate of proton exchange in hydrogen bond chains of the KHSeO₄ (straight line 1) and NH₄HSeO₄ (straight line 2) crystals [1] are plotted in Fig. 3. It can be seen from this figure that both the rates and the activation energies of deuteron exchange in these crystals nearly coincide. However, the magnitude of the electrical conductivity in the PHS crystal is approximately 100 times less than that in the AHS crystal at the same temperature (Fig. 4). It should also be noted that no considerable conductivity anisotropy is observed for the PHS crystal (Fig. 4), even though this anisotropy can be

expected with due regard for the relative isolation of the layers composed of hydrogen bond chains.

It follows from the structural data obtained by Aleksandrov et al. [6] that, in the paraelectric phase of the AHS crystal, the shortest distance separating the protons in equivalent positions is equal to the unit cell parameter b (4.61 Å). This distance exceeds the shortest distance (3.91 Å) between the positions of protons in the adjacent chains of the hydrogen bonds. In the neighboring tetrahedra SeO₄ of different chains, the shortest distance between the oxygen atoms, which are not involved in the formation of hydrogen bonds, is approximately equal to 3.3 Å. Moreover, protons can occupy vacant positions between oxygen atoms separated by a distance of 3.18 Å. Therefore, the number of vacant positions in the paraelectric phase of the AHS crystal is considerably larger than the number of protons. As a result, hydrogen bonds with a short lifetime can be formed between the appropriate oxygen atoms. The main mechanism of proton transport in the paraelectric phase of the AHS crystal is associated with the proton hopping between the adjacent chains of the hydrogen bonds. A drastic increase in the electrical conductivity of the AHS crystal at temperatures above 417 K is caused by the disordering of the oxygen atoms of the SeO₄ groups in the superionic phase. In this case, the number of possible relative positions of the oxygen atoms in the SeO₄ groups and the number of possible positions of the protons in the hydrogen bonds considerably increase as compared to those in the paraelectric phase. As a consequence, the electrical conductivity of the high-temperature phase increases abruptly. According to the ²H NMR data [1], all protons of the hydrogen bonds in the superionic phase are described by a sole averaged electric-field gradient tensor. This suggests a high diffusive mobility of these protons.

The distance between chains in the PHS crystal is approximately identical to that in the AHS crystal. However, the distance between the oxygen atoms that belong to the adjacent chains and do not participate in the formation of hydrogen bonds in the former crystal owing to the presence of the dimer layers is substantially larger than the corresponding distance in the latter crystal. The O1–O2 and O3–O4 distances are larger than 3.9 and 4.2 Å, respectively (Fig. 2a). Only the O2–O5 distance equal to 3.565 Å is comparable to the corresponding distance in the AHS crystal. Therefore, the number of vacant positions of protons in the PHS crystal is small and they do not form a connected network for paths of proton motion in the crystal. The proton hopping between the adjacent chains of hydrogen bonds clearly manifests itself in our NMR spectra [1] and is local in character. It is interesting to note that, if the proton transfer occurs through reorientation of the SeO₄ groups, as was assumed in [7, 8], the observed proton hopping between the adjacent chains of hydrogen bonds should lead to the appearance of an electrical conductivity (in the chain plane) comparable to the

electrical conductivity in the AHS crystal at close rates of proton exchange.

As was noted above, the electrical conductivity in the PHS crystal is nearly 100 times lower than that in the AHS crystal (Fig. 4). The estimates demonstrate that the rates of proton exchange responsible for this conductivity do not exceed 100 s^{-1} at temperatures as high as 400 K. These slow processes cannot be revealed from a change in the one-dimensional ^2H NMR spectra, because the linewidth is considerably larger than the above value [1]. In order to obtain information on these slow processes, we used two-dimensional ^2H NMR spectroscopy. The mathematical formalism of the chemical exchange processes and calculations of the rates of proton exchange from two-dimensional NMR spectra have been considered in a number of well-known works [9, 10] and were briefly described in our previous papers [1–4]. The chemical exchange can be represented by the basic equation (see, for example, [11])

$$\frac{\partial n_i}{\partial t} = \sum_j^n p_{ij} n_j, \quad (1)$$

where p_{ij} is the probability of transfer from the i th position to the j th position and n_j is the occupancy of the j th position. In the matrix form, Eq. (1) is written as $\dot{\mathbf{n}} = \mathbf{p}\mathbf{n}$ with the solution

$$\mathbf{n}(t) = \exp(\mathbf{p}t)\mathbf{n}_0 = \mathbf{A}(t)\mathbf{n}_0. \quad (2)$$

Here, the components n_{0i} of the vector $\mathbf{n}_0 = \{n_{01}, \dots, n_{0i}\}$ are equal to the number of deuterons in the i th position at the instant of time $t = 0$ and the components n_i of the vector $\mathbf{n}(t) = \{n_1, \dots, n_i\}$ are equal to the number of deuterons in the same position at the instant $t = \tau_m$. The components $A_{ij}(t)$ of the exchange matrix $\mathbf{A}(t)$ in relationship (2) completely determine the kinetics of deuteron (proton) exchange in the crystal and can be obtained from the intensities of the corresponding off-diagonal peaks in the two-dimensional ^2H NMR spectra [9, 10]. The two-dimensional ^2H NMR experiments with the PHS crystal were performed in the temperature range 375–400 K for the crystal orientation where the \mathbf{b} axis is perpendicular to the external magnetic field \mathbf{B}_0 and the angle between the \mathbf{a} axis and the vector \mathbf{B}_0 is equal to 40° . For the given orientation, the NMR spectrum is characterized by the best resolution and the minimum total width. These conditions ensure a considerable decrease in the time of recording the two-dimensional NMR spectra. Figure 5 shows the left upper quadrant of the typical two-dimensional ^2H NMR spectrum of the PHS crystal (at a temperature of 400 K and a mixing time of 20 ms). The off-diagonal peaks in Fig. 5 indicate deuteron exchange between hydrogen bond chains and dimers and between magnetically non-equivalent positions of deuterons of the dimers. Unlike the AHS crystal [2–4] and PHS crystal at low tempera-

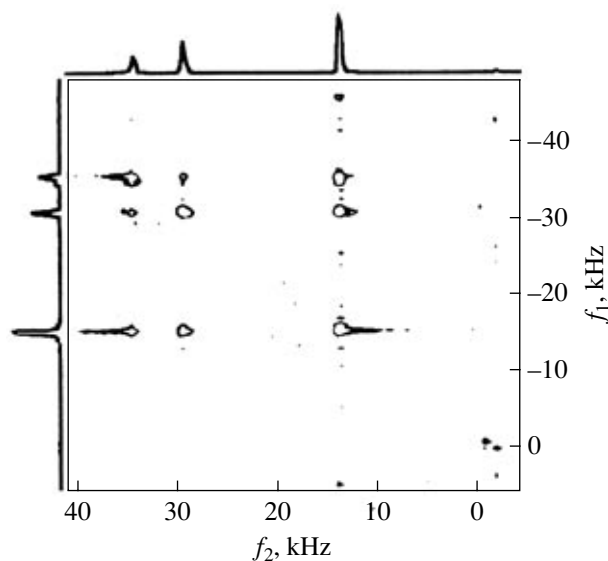


Fig. 5. Two-dimensional ^2H NMR spectrum of the PHS crystal at a temperature of 400 K and a mixing time of 20 ms (left upper quadrant).

tures (up to 350 K) [1], the exchange in the PHS crystal at the temperatures under investigation involves three different structural positions. In this case, in order to determine the rates of these processes, it is necessary to examine the dependence of the intensity of the off-diagonal peaks on the mixing time. It should be noted that, in the study of such slow processes at high temperatures, the mixing time is comparable to the spin–lattice relaxation time. This fact was taken into account when analyzing the two-dimensional NMR spectra. In order to increase the measurement accuracy, the data were averaged over all four quadrants of the two-dimensional spectrum. It is well known [9, 10] that the off-diagonal peaks in two-dimensional NMR spectra appear as a result of both direct and indirect exchanges. However, the dependences of the intensity of the off-diagonal peaks on the mixing time for these processes are different. The analysis shows that the rate of indirect deuteron exchange between magnetically non-equivalent positions of dimers is very low up to a temperature of 400 K (0.3 s^{-1} at 375 K, 0.6 s^{-1} at 385 K, and 5 s^{-1} at 400 K). Figure 3 (straight line 3) depicts the temperature dependence of the rate of direct deuteron exchange between chains and dimers according to the data of two-dimensional NMR spectroscopy. This dependence was approximated by the Arrhenius equation; that is,

$$p(T) = p_0 \exp(E_a/RT). \quad (3)$$

As a result, we determined the activation energy of this process (it is approximately equal to 120 kJ/mol). The activation energy thus obtained is in good agreement with the activation energy calculated from the temperature dependence of the electrical conductivity of the

PHS crystal (Fig. 4). The electrical conductivities estimated from the data obtained and the known structural parameters with the use of the Nernst–Einstein relationship turn out to be close to the experimental results.

4. CONCLUSIONS

Thus, it has been established that the deuteron exchange between layers formed by hydrogen bond chains and dimers is a necessary condition responsible for the proton transport in the PHS crystal. The rate and activation energy of this process determine the macroscopic characteristics of the electrical conductivity in the crystal.

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