Abstract—The chemical exchange of deuterons in a partly deuterated ammonium hydrogen selenate crystal is investigated by deuteron magnetic resonance (\(^{2}\text{H} \text{NMR}\)) spectroscopy over a wide range of temperatures. The changes observed in the line shape of the NMR spectra at temperatures above 350 K are characteristic of chemical exchange processes. The exchange processes are thoroughly examined by two-dimensional \(^{2}\text{H} \text{NMR}\) spectroscopy. It is established that, over the entire temperature range, only deuterons of hydrogen bonds are involved in the exchange and the rates of exchange between deuterons of all types are nearly identical. No deuteron exchange between the ND\(_{3}\) groups and hydrogen bonds is found. A new model of proton transport in ammonium hydrogen selenate is proposed on the basis of the experimental data. This model makes it possible, within a unified context, to explain all the available experimental data, including macroscopic measurements of the electrical conductivity.

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1. INTRODUCTION

Considerable recent interest expressed by researchers in crystals with a high ionic conductivity stems from both important practical applications of these compounds and the basic problems concerning electrical conductivity in superionic crystals [1–4]. In this respect, crystals whose structure involves quasi-one-dimensional chains of hydrogen bonds are of particular importance. These crystals are good model objects for use in verifying different assumptions on microscopic mechanisms of ionic conductivity. Ammonium hydrogen selenate (AHS) \(\text{NH}_4\text{HSeO}_4\) belongs to these crystals. In the structure of AHS crystals, infinite quasi-one-dimensional chains are formed by SeO\(_4\) tetrahedra joined through protons of hydrogen bonds. The deuteration of AHS makes it possible to apply the powerful method of nuclear magnetic resonance (NMR) at quadrupole nuclei to perform research into proton (deuteron) transport. In addition to conventional Fourier-transform NMR spectroscopy, elementary processes of deuteron chemical exchange have been investigated by two-dimensional (2D) NMR spectroscopy. As a rule, the 2D NMR data are compared with the results of dielectric measurements performed over a wide range of frequencies (10\(^{-2}\)–10\(^{10}\) Hz). Dielectric measurements at very low frequencies permit one to increase appreciably the accuracy in determination of the dc conductivity \(\sigma_{dc}\) and to compare quantitatively the results of dielectric and NMR measurements for AHS crystals. The structure and properties of AHS single crystals have been described thoroughly in our earlier works [4–7].

In the present work, we analyzed our results with the aim of elucidating the microscopic mechanism of proton transport in AHS crystals.

2. SAMPLE PREPARATION AND EXPERIMENTAL TECHNIQUE

Partly deuterated (25\%) AHS crystals were grown from an aqueous solution containing an excess of H\(_2\)SeO\(_4\) and the appropriate amount of heavy water. Protons involved both in ammonium groups and in hydrogen bonds were partly replaced by deuterons. The degree of deuteration was chosen reasoning from the specific features of the phase diagram of the NH\(_4\)HSeO\(_4\) compound, which, at a growth temperature of 30\(^{0}\)C and a degree of deuteration higher than 45\%, crystallizes in another phase [8]. The nuclear magnetic resonance and dielectric measurements were performed with the same samples. The \(^{2}\text{H} \text{NMR}\) 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\(^{0}\) pulse was equal to approximately 4 \(\mu\)s. A spin echo sequence with a time interval of 25 \(\mu\)s between pulses was used in order to exclude the effect of the dead time of the NMR spectrometer receiver. Moreover, proton decoupling was applied to suppress the broadening of \(^{2}\text{H} \text{NMR}\) lines due to the dipole–dipole interaction with the remaining protons. The two-dimensional NMR measurements were performed using the following spin echo sequence: \((\pi/2)_{x}–t_{1}–(\pi/2)_{y}–\tau_{m}–(\pi/2)_{x}–\tau–(\pi/2)_{y}–\tau–t_{2}\), where \(t_{1}\) is the evolution time, \(t_{2}\) is the measurement interval of 25 \(\mu\)s between pulses was used in order to exclude the effect of the dead time of the NMR spectrometer receiver.
time, τ is the time interval between pulses, and τ_m is the mixing time. The dielectric susceptibility was measured on a Schlumberger Solartron 1255 HF Frequency Response Analyzer in the frequency range from 10^{-2} to 10^6 Hz. Samples approximately 0.8 mm thick were cut from the AHS single crystal. For dielectric measurements, electrodes were prepared in the form of thin gold films applied to the sample surface under vacuum.

3. RESULTS AND DISCUSSION

The most interesting features inherent in the AHS crystal are as follows: the ferroelectric state associated with ordering of protons involved in hydrogen bonds, the incommensurate phase [6, 7], and the protonic conductivity [1–3]. In the paraelectric phase, the AHS crystal is characterized by a monoclinic unit cell with space group B2 and the lattice parameters a = 19.745 Å, b = 4.611 Å, c = 7.552 Å, and γ = 102.56° [9]. The crystal structure is built up of SeO_4^{2–} tetrahedral ions joined by hydrogen bonds into infinite chains aligned along the ferroelectric axis b (Fig. 1). The SeO_4 groups are linked by ammonium ions along the two other axes a and c. Hydrogen bonds between the different structural groups SeO_4 considerably differ from each other. The length of the hydrogen bonds between the Se(1)O_4 groups (α bonds) is equal to 2.56 Å, and the length of the hydrogen bonds between the Se(2)O_4 groups (β bonds) is 2.59 Å (Fig. 1). In the paraelectric phase, protons of the α bonds are disordered dynamically [6, 7].

Reasoning from the analysis of the 1H NMR spectra and measurements of the 1H spin–lattice relaxation time, Moskvich et al. [1] assumed that the isotropic diffusive motion of ammonium groups and protons of hydrogen bonds occurs in the paraelectric phase. These authors proposed a microscopic mechanism of proton transport through a correlated reorientation of SeO_4 groups with a sequential exchange of protons between SeO_4 groups along an infinite chain of hydrogen bonds. In this case, the activation energy for reorientational motion of SeO_4 groups is a controlling factor of the proton hopping rate. It should be noted that the activation energy for reorientational motion of SeO_4 groups is approximately equal to the activation energy for isotropic diffusion of ammonium groups which contribute significantly to the electrical conductivity of the crystal [1, 2]. However, for the most part, all these assumptions are based on analyzing the temperature dependence of the second moment (linewidth) of the 1H NMR spectra. It is known that, over the entire temperature range, the 1H NMR spectrum consists of a single line whose second moment is predominantly determined by the dipole–dipole interactions between protons of ammonium groups [1]. In our opinion, these investigations cannot provide detailed information on the microscopic mechanism of proton transport in the AHS crystal.

In this work, the microscopic characteristics of ammonium hydrogen selenate are determined from the 1H NMR spectra of a partly deuterated AHS crystal. Unlike protons, deuterium nuclei possess a quadrupole moment. Nuclear magnetic resonance at quadrupole nuclei provides valuable information on the magnitude and symmetry of crystal-electric-field gradients at the studied nucleus. For a strong external magnetic field B_0, when the Zeeman interaction energy substantially exceeds the energy of interaction between the nuclear quadrupole moment and the crystal field, the crystal field brings about a perturbation of equidistant Zeeman levels and a splitting of the NMR line into 2I components (I is the nuclear spin), which are symmetrically located with respect to the Larmor precession frequency ν_0 in the magnetic field B_0 [10]. Consequently, the NMR spectrum of deuterons (I_p = 1) consists of doublets whose number for a single-crystal sample in the general case is equal to the number of magnetically nonequivalent deuterium nuclei. According to Pound [10], the quadrupole splitting (ν_2 − ν_1) can be represented by the relationship

\[ ν_2 − ν_1 = \frac{6eQ}{4h} V_{zz}^{LAB} = Φ_{zz}, \]

where Q is the nuclear quadrupole moment, e is the elementary charge, h is the Planck constant, and V_{zz} is the zth component (the magnetic field B_0 is aligned along the z axis) of the electric-field gradient at the nucleus. All the components V_{ij} of the electric-field gradient tensors for each structurally nonequivalent position of deuterium in the crystal in the laboratory coordinate system can be determined from the orientation dependencies of the quadrupole splitting within the framework of the well-known Volkoff method [11]. The elect-

Fig. 1. Structure of NH_4HSeO_4 in the paraelectric phase. A half of the unit cell is shown. Wavy lines indicate hydrogen bonds between the oxygen atoms of the SeO_4 groups.