

# NMR Spectra and Translational Diffusion of Protons in Crystals with Hydrogen Bonds

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**Abstract**—Investigation of proton transport in hydrogen-bond crystals at low temperatures is currently one of important problems in the semiconductor physics. With the use of the NMR spectra of wide-band-gap hydrogen-bond crystals grown in H<sub>2</sub>O and D<sub>2</sub>O solutions, we have succeeded in finding a direct proof of the presence of protons in the mobile phase, determined their activation energy in good agreement with the spectra of thermally stimulated depolarization currents and with the infrared spectra, and, as a result, clarified the mechanism of proton transport and tunneling.

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## 1. INTRODUCTION

The dynamics of protons of hydrogen bonds at low temperatures has been poorly studied despite a large number of works, since investigations have been basically carried out at high temperatures in liquid and solid electrolytes and in a few crystals of the type of ammonium hydroselenate NH<sub>4</sub>HSeO<sub>4</sub> [1], the structure of which includes hydrogen-bonded chains. To study the mechanism of dielectric relaxation and electrical conduction of wide-band-gap ionic crystals at low temperatures, we explored their characteristics, namely, the dielectric losses  $\tan\delta(\nu, T)$ , electrical conductivity, and thermally stimulated depolarization currents. The regularities inherent only to hydrogen-bond crystals were discovered. In the previous work of one of us [2], the mechanism of hopping diffusion of protons was proposed, but the presence of tunneling and translational diffusion of protons could not be asserted with a high accuracy based only on electrical measurements. To check this statement, we measured infrared (IR) transmission and absorption spectra [3] and to confirm the presence of protons in a mobile phase, we studied the NMR spectra of protons. We investigated flaky mica crystals (muscovite KAl<sub>2</sub>[AlSi<sub>3</sub>O<sub>10</sub>][OH]<sub>2</sub> and phlogopite KMg<sub>3</sub>[AlSi<sub>3</sub>O<sub>10</sub>][F,OH]<sub>2</sub>) widely used as electric insulation materials and lithium iodate crystals in the hexagonal modification  $\alpha$ -LiIO<sub>3</sub> used in

laser technologies and fiber-optic communication lines. All these crystals include hydrogen bonds to some extent.

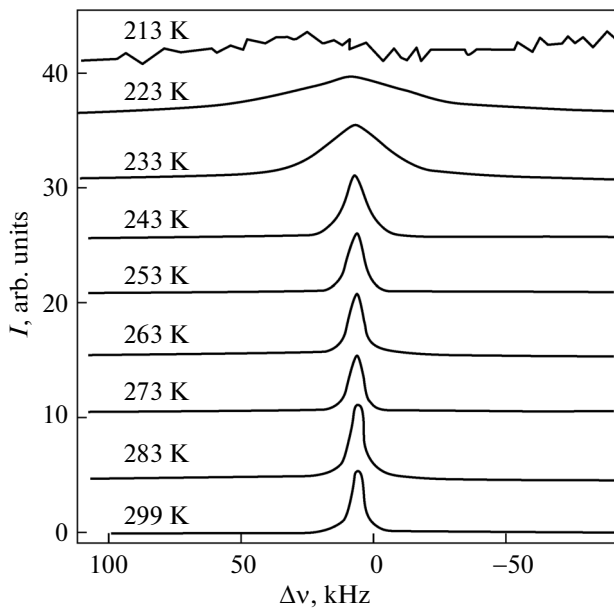
## 2. SAMPLE PREPARATION, EXPERIMENTAL TECHNIQUE, AND RESULTS

In [3], we found the band gaps for  $\alpha$ -LiIO<sub>3</sub> ( $E_g = 4.46$  eV) and silicate (phlogopite and muscovite,  $E_g = 4.31$  eV) single crystals. Consequently, electron transitions from the valence band to the conduction band at low temperatures can be excluded for silicates and lithium iodate. This would require a temperature of a few thousand Kelvin. This confirms that translational diffusion and tunneling at low temperatures (about 170–77 K and below) are possible only for protons. In this work, we showed that the IR spectra of the crystals under investigation contain protons and proton defects in the mobile phase, which form absorption centers, whereas deuterons do not form such centers owing to a low mobility.

Investigation of the proton NMR spectra of lithium iodate crystals grown in ordinary and heavy water was carried out on a Bruker AVANCE IIIITM 300 spectrometer at a Larmor frequency of 46.073 MHz. The line widths of the spectra of the crystals grown in H<sub>2</sub>O (Fig. 1) are listed in the table. The proton signals were

Line width  $\Delta\nu$  (kHz) of the proton NMR spectrum of lithium iodate crystals

299 K	283 K	273 K	263 K	253 K	243 K	233 K	223 K	213 K
1.65 ± 0.05	1.67 ± 0.05	1.76 ± 0.05	2.05 ± 0.05	2.16 ± 0.05	3.3 ± 0.1	8.10 ± 0.1	17.5 ± 0.2	27.0 ± 5

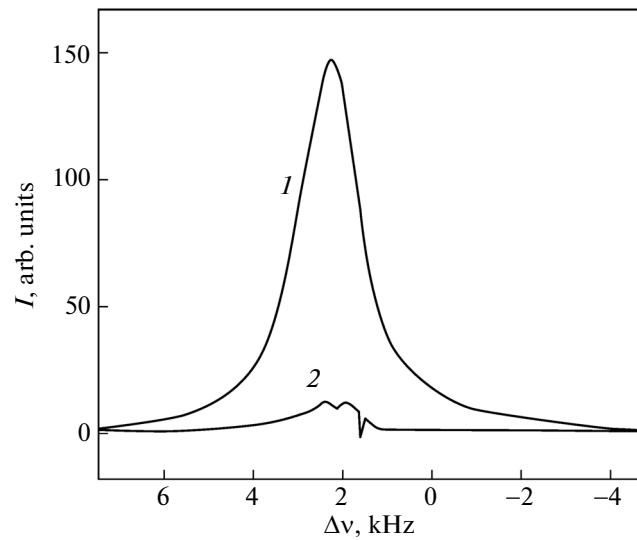


**Fig. 1.** Proton NMR spectrum of  $\alpha$ -LiIO<sub>3</sub> crystals along the  $C_6 [000\bar{1}]$  axis. The crystals were grown in H<sub>2</sub>O.

detected under the following conditions: the frequency of 300 MHz with a frequency sweep of 60 kHz, the number of scans of 200, the excitation pulse length of 4 s, the delay time of 0.2 s, and the dead time of 12  $\mu$ s. A 15  $\times$  4  $\times$  2-mm crystal was oriented in such a way that the  $C_6 [000\bar{1}]$  axis was perpendicular to the magnetic field. All measurements were performed with the subtraction of the background signal.

As is seen in Fig. 1, the line width increases significantly at temperatures below 213 K. This is associated with the fact that oscillations of protons and proton defects H<sub>3</sub>O<sup>+</sup> and OH<sup>-</sup> are frozen out so that their mobility decreases. It is exactly this temperature, at which a change in the slope of the temperature dependence of the electrical conductivity  $\log \sigma = f(1/T)$ , i.e., a change in the mechanism of electrical conduction, which is essentially caused by tunneling of protons at low temperatures. In addition, the NMR spectrum of protons in a deuterated  $\alpha$ -LiIO<sub>3</sub> crystal (Fig. 2, curve 2) exhibits a double line manifesting the presence of two types of nonequivalent protons that can belong to H<sub>3</sub>O<sup>+</sup> and OH<sup>-</sup> ions. Curve 1 in Fig. 2 is shown for comparison and corresponds to the line at  $T = 299$  K in Fig. 1; its height is magnified by a factor of 30 with respect to Fig. 1.

Two slopes of the dependence  $\ln \Delta \nu = f(1/T)$  (Fig. 3), where  $\Delta \nu$  is the FWHM, obtained from the NMR spectra yielded two activation energies  $\Delta E_a$  of protons: an energy of 0.054 eV coinciding with the activation energy of the first maximum of the thermally stimulated depolarization current ( $T = 112$  K) caused by relaxation of the anions HIO<sub>3</sub> and tunneling

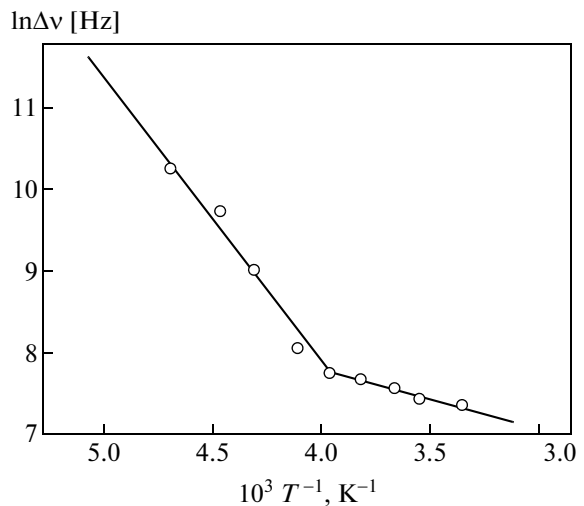


**Fig. 2.** Proton NMR spectrum of  $\alpha$ -LiIO<sub>3</sub> crystals along the  $C_6 [000\bar{1}]$  axis. The crystals were grown in (1) H<sub>2</sub>O and (2) D<sub>2</sub>O.  $T = 299$  K.

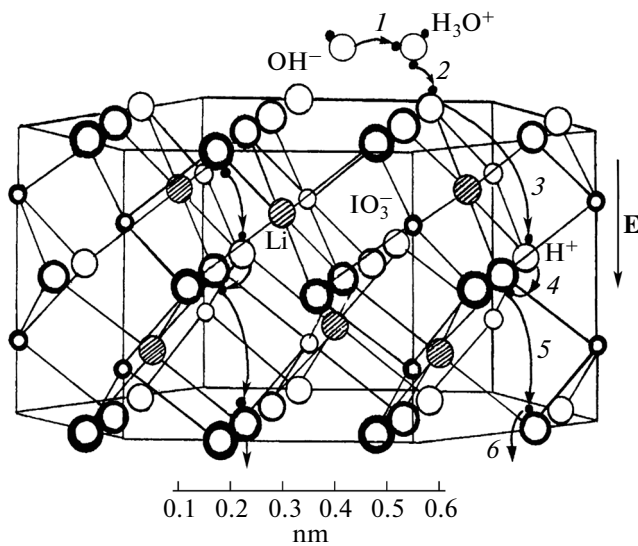
transitions of protons between oxygen ions and an energy of 0.31 eV coinciding with the activation energy of third maximum of the thermally stimulated depolarization current ( $T = 190$  K) associated with relaxation of crystal water molecules, which are basic for the formation of the defects H<sub>3</sub>O<sup>+</sup> and OH<sup>-</sup> [2]. Similar lines corresponding to these ions are also present in the IR spectra [3].

The resonance frequency in hertz is defined as [4]

$$\nu_0 = \frac{\gamma B_0}{2\pi},$$



**Fig. 3.** Arrhenius plot of the temperature dependence of the proton NMR line width.



**Fig. 4.** Scheme of the motion of a  $\text{H}_3\text{O}^+$  ion via translational (hopping) diffusion of a proton in  $\alpha\text{-LiIO}_3$  crystals. Arrows and numbers mark the stages of the proton motion.

where  $\gamma$  is the gyromagnetic ratio. For protons,  $\gamma = 42.58 \text{ MHz T}^{-1}$ , thus, one can write for the crystal lattice in the field, e.g.,  $B_0 = 1.41 \text{ T}$

$$\Delta\nu = \gamma\Delta B_0/2\pi. \quad (1)$$

Taking for an estimate the distance between the nuclei of the lithium iodate crystal on the order of the lattice parameter (0.548 nm) and the nuclear magnetic moment equal to one nuclear magneton  $\mu_N = eh/4\pi m_p = 5.0505 \times 10^{-27} \text{ J/T}$ , we find the local magnetic fields of the neighboring nuclei to be  $B_0 \sim \mu r^{-3} \approx 0.63 \times 10^{-4} \text{ T}$ . According to Eq. (1), this leads to the NMR line width  $\Delta\nu \approx 2.5 \text{ kHz}$ , which is confirmed by our measurements. In this case, the translational mobility of protons can be found with the use of the expression

$$\mu = \frac{a^2 q v_0}{kT} \exp\left(-\frac{\Delta E_a}{kT}\right).$$

Here,  $a \approx 2 \text{ \AA}$  is the distance between the adjacent positions of a proton in the lattice structure, which ranges from 1.215  $\text{\AA}$  in the tetrahedron  $[\text{SiO}_4^{4-}]$  to 2.19  $\text{\AA}$  in lithium iodate crystals;  $v_0 = 2 \times 10^{13} \text{ s}^{-1}$  is the proton hopping frequency; and  $\Delta E_a = 0.054 \text{ eV}$ . The mobility at  $T = 300 \text{ K}$  is  $3.83 \times 10^{-6} \text{ m/(V s)}$ .

### 3. DISCUSSION OF THE RESULTS

As was shown in [5], the transmittance of a 1.2- $\text{\AA}$ -wide potential barrier for proton tunneling is  $D = 0.0075$ . This is a noticeable quantity, since the concentration of proton-containing defects  $\text{H}_3\text{O}^+$ ,  $\text{OH}^-$ ,  $\text{H}_2\text{O}$

and protons themselves is about  $10^{21} \text{ m}^{-3}$ . Oxygen atoms in  $\text{LiIO}_3$  crystals form a hexagonal packing with a density of 50% and iodine atoms occupy octahedral voids forming separate  $\text{IO}_3$  groups. Proton as an atom without an electronic shell cannot exist in a free form. It is trapped by an electronegative oxygen atom in tetrahedra  $[\text{SO}_4^{2-}]$  (sulfates),  $[\text{SiO}_4^{4-}]$  (silicates) or octahedra  $[\text{IO}_3^-]$  (iodates). In this case, the proton trapped into the electronic shell of the oxygen atom decreases its size with the formation of the  $\text{OH}^-$  group ( $r(\text{O}_2^-) = 0.14 \text{ nm}$ ,  $r(\text{OH}^-) = 0.137 \text{ nm}$ ). However, one has to take into account that the proton–oxygen bond is weaker than in the hydroxyl ion  $\text{OH}^-$  and, since coupling of oxygen to the lattice is stronger than that of hydrogen, the latter migrates across the crystal as an individual proton rather than as an  $\text{OH}^-$  ion, let alone a  $\text{H}_3\text{O}^+$  ion.

The analysis of the NMR spectra taking into account the thermally stimulated depolarization current,  $\tan\delta(\nu, T)$  and IR spectra of a set of crystals allowed finding a direct proof of the existence of protons in the mobile phase and revealing the mechanism of dielectric relaxation and proton transport along the  $C_6 [000\bar{1}]$  axis in the direction of the polarizing field in crystalline materials, which includes 6 stages (Fig. 4).

**Stage 1.** As a result of displacement of protons along the hydrogen bond from one  $\text{H}_2\text{O}$  molecule to another,  $\text{H}_3\text{O}^+$  defects appear, which is also possible by embedding proton-donor impurities of the HCl type. The concentration of the  $\text{H}_3\text{O}^+$  defects increases owing to substitution of the oxygen ion by chlorine possessing a lower valence; as a result, one proton is released and an  $L$  defect (an empty valence bond) is created. The proton departs from the chlorine atom toward the neighboring water molecule and forms a  $\text{H}_3\text{O}^+$  defect (e.g., via  $\text{HCl} + \text{H}_2\text{O} \leftrightarrow \text{Cl}^- + \text{H}_3\text{O}^+$ ).

**Stage 2.** Translational (hopping) diffusion of a proton from the  $\text{H}_3\text{O}^+$  ion to the  $\text{IO}_3^-$  anion occurs in the first layer of lithium iodate crystals with the formation of a protonated  $\text{HIO}_3$  anion (e.g., via  $\text{H}_3\text{O}^+ + \text{IO}_3^- \rightarrow \text{H}_2\text{O} + \text{HIO}_3$ ).

**Stage 3.** Next, the created protonated anion changes its orientation owing to the tunneling transition of the proton to the adjacent oxygen ion inside the anion with an activation energy of 0.05–0.06 eV:  $\text{HIO}_3 \rightarrow \text{IO}_3\text{H}$ .

**Stage 4.** Transition of the proton between  $[\text{IO}_3^-]$  octahedrons to the next layer of the anionic sublattice can proceed via thermally activated manner and by tunneling, in which case the newly formed protonated anion acquires the opposite orientation:  $\text{IO}_3\text{H} \rightarrow \text{HIO}_3$ .

**Stage 5.** Spontaneous reorientation of the  $\text{IO}_3^-$  anion in the second layer is energetically forbidden; it is only possible via the tunneling transition of the proton to the adjacent oxygen ion:  $\text{HIO}_3 \rightarrow \text{IO}_3\text{H}$ .

**Stage 6.** Translational (hopping) diffusion of the proton to a water molecule and the creation of a  $\text{H}_3\text{O}^+$  defect occurs according to the scheme  $\text{IO}_3\text{H} + \text{H}_2\text{O} \rightarrow \text{IO}_3^- + \text{H}_3\text{O}^+$ .

Similar transitions occur in tetrahedra of sulfates [ $\text{SO}_4^{2-}$ ] and silicates [ $\text{SiO}_4^{4-}$ ] and in other hydrogen-bond crystals.

#### 4. CONCLUSIONS

Investigation of the NMR spectra confirmed the existence of directed translational diffusion and tunneling of protons and proton defects in the lattice structure of crystalline materials with hydrogen bonds at low temperatures. The analysis of the electrical conductivity, as well as the NMR and IR spectra, showed that the character of conductivity changes from thermally activated to tunneling at temperatures below 213 K. Apparent motion of  $\text{H}_3\text{O}^+$  ions occurs via the hopping diffusion and tunneling of protons.

Based on the studied mechanisms of proton transport and tunneling, we have elaborated:

(i) physical foundations of a technology of fabrication and diagnostics of proton conductors and semiconductors of  $n$  and  $p$  types [2];

(ii) the method of measuring the temperature of the tunnel effect in dielectrics and electrically insulating materials [6];

(iii) the method of determining the concentration and type of relaxators in crystalline materials [7] and other methods and technologies.

These methods and technologies are associated with both fundamental and technical solutions directed to the development of the methods of diagnostics and optimization of the parameters of optical and electrotechnical materials and products, improvement of existing materials, and creation of new laser and electrically insulating materials, electric insulation and cables with high durability, technological efficiency, and operational safety.

#### REFERENCES

1. Yu. N. Ivanov, A. A. Sukhovskii, I. P. Aleksandrova, J. Totz, and D. Michel, *Phys. Solid State* **44** (6), 1077 (2002).
2. V. M. Timokhin, RF Patent No. 2360239, *Byull. Izobret.*, No. 18 (2009).
3. V. M. Timokhin, V. M. Garmash, and V. A. Tedzhetov, *Sovrem. Probl. Nauki Obraz., Elektron. Zh.*, No. 3 (2013). <http://www.scienceeducation.ru/109-9597>.
4. A. G. Lundin and V. E. Zorin, *Phys.—Usp.* **50** (10), 1053 (2007).
5. V. M. Timokhin, *J. Nano- and Electron. Phys.* **6** (3), 03048 (2014).
6. V. M. Timokhin, RF Patent No. 2347216, *Byul. Izobret.*, No. 5 (2009).
7. V. M. Timokhin, RF Patent No. 2478199, *Byull. Izobret.*, No 9 (2013).

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