

A.I. OVCHARENKO, E.D. CHESNOKOV, I.G. VERTEGEL, L.S. IVANOVA,
YU.P. GNATENKO

Institute of Physics, Nat. Acad. of Sci. of Ukraine
(46, Nauky Ave., Kyiv 03680, Ukraine)

**INFLUENCE OF PROTON EXCHANGE
ON NMR RELAXATION MECHANISM OF ${}^7\text{Li}$**

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The temperature dependence of the ${}^7\text{Li}$ spin-lattice relaxation time in the temperature interval 170–340 K has been studied in undoped and proton-exchanged powder specimens of LiNbO_3 . An anomaly in the temperature behavior of the relaxation time T_1 in the temperature interval 300–340 K is revealed in both specimens, which is related to the local lattice reconstruction. On the basis of the activation energy values calculated from the $T_1(T)$ dependence, a conclusion is made that the dominant relaxation mechanism in the considered temperature interval is the tunneling of Li ions between sublattice vacancies. The difference between the activation energies for two polycrystals is explained by the transition from a symmetric three-well potential to an asymmetric one owing to the appearance of oxygen vacancies and the localization of impurity protons in the oxygen plane.

Keywords: method of nuclear magnetic resonance, proton exchange, relaxation.

In recent years, crystals of lithium niobate, LiNbO_3 , owing to their optical, piezoelectric, and pyroelectric properties, have found a rather wide application in modern devices of nonlinear optics, electroacoustic units, and other branches of the scientific instrument engineering [1]. However, laser irradiation of those crystals gives rise to the so-called optical damage associated with a change of the refractive index [2, 3], which imposes restrictions on their application. A study of this phenomenon revealed the influence of the impurities and intrinsic or introduced defects on this effect [4, 5]. The corresponding researches showed that the optical stability of lithium niobate can be enhanced by doping it with magnesium [6, 7] or filling the lithium vacancies with protons by annealing pure LiNbO_3 in the hydrogen atmosphere at high temperatures [8, 9].

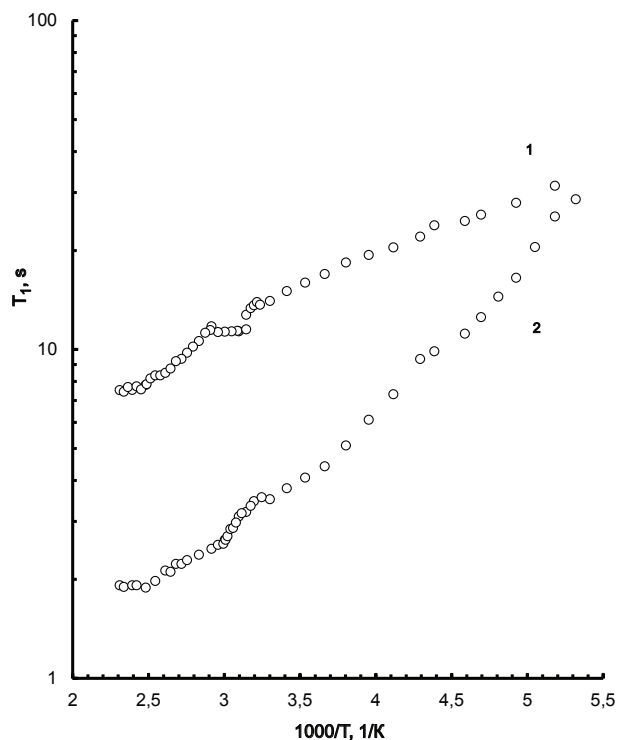
When researching ferroelectrics, including lithium niobate, the method of nuclear magnetic resonance

(NMR) spectroscopy is widely used, which has rather a high efficiency for the study of crystal structures, intracrystal field distributions, and the perfection degree of crystal lattices [10–12]. In addition, the nuclear magnetic resonance provides another, rather informative technique to study both the structural and dynamic characteristics of crystals. It consists in the research of processes associated with nuclear spin-lattice relaxation (SLR). The corresponding SLR time T_1 is proportional to the correlation time τ_c , which characterizes, in the case of thermally activated process, the activated jumps over the vacancies in the crystal lattice according to the Arrhenius relation

$$\tau_c = \tau_0 \exp(E_a/kT),$$

where E_a is the activation energy for the dominating motion type. Therefore, the study of the temperature dependence of T_1 allows one to find the activation energy, estimate the probability for that or another relaxation mechanism, and, hence, determine the dominating type of motion for the examined nucleus or ion.

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I.G. VERTEGEL, L.S. IVANOVA,
YU.P. GNATENKO, 2015



Dependence of the SLR time on the inverse temperature in the initial (1) and annealed (2) specimens of lithium niobate

However, SLR researches of LiNbO_3 crystals were sporadic [13–15] and mainly concerned the high-temperature interval (300–1400 K). In the researches dealing with the SLR and the dynamics of a lattice in pure and undoped LiNbO_3 crystals, it was demonstrated that, at high temperatures exceeding 500 K, the dominating mechanism of relaxation of ^7Li nuclei is the hopping diffusion of lithium nuclei with a high activation barrier (about 1 eV) [13, 15]. At the same time, the character of motion of lithium nuclei in the interval of temperatures at which LiNbO_3 -based devices are exploited remained obscured.

Researches of lithium niobate doped with H^+ ions (protons) using various methods including the NMR spectroscopy [16–19] revealed that if the initial LiNbO_3 is annealed in an environment containing hydrogen, protons occupy lithium vacancies in the oxygen plane between two oxygen anions. However, the data concerning the SLR mechanisms and the dominating types of motion in such crystals are practically absent. That is why the researches of SLR

in pure and proton-exchanged lithium niobate crystals aimed at detecting the difference between those cases and elucidating the influence of the proton exchange on the dynamics features of lithium nuclei are challenging.

We studied the temperature dependences of T_1 for ^7Li nuclei in the intermediate temperature interval (170–430 K) for polycrystalline LiNbO_3 specimens ground to the powder state and after their annealing in a hydrogen-containing environment for 6 h at a temperature of 1000 °C. The SLR studies of ^7Li nuclei were carried out on a radiospectrometer ISSh-2-13 with the use of a “Tesla BS 488” electromagnet at a frequency of 11.7 MHz. In our researches, we followed the standard $90^\circ - \tau - 90^\circ$ pulse technique. The determination accuracy for the time T_1 amounted to 7%. A thermostat system made it possible to maintain the specimen temperature to an accuracy of ± 0.5 K in the whole interval of researched temperatures. The determination accuracy for the activation energy was 10%.

The experimental results are shown in Figure. An anomaly in the temperature interval 300–340 K was found in the temperature dependences $T_1(T)$ for both the initial and annealed polycrystalline specimens. Both above and below the indicated temperature interval, the relaxation has a thermally activated character, but with different activation barriers. Proceeding from such a variation, the anomalies in the temperature dependence of the SLR time can be explained by local distortions of a crystal structure in the temperature interval 300–340 K. As a result, the activation barriers change for all types of relaxing nuclei.

Earlier, changes in the NMR spectra of ^7Li in the lithium niobate powder were found in the same temperature interval [20]. The cited authors associated them with the existence of two phases characterized by different values of the ratio between the lattice parameters c/a . This explanation agrees with the results of previous x-ray diffraction researches [21] carried out with the participation of the authors of work [20]. The variation of the axial ratio between the lattice parameters c/a may be related to the temperature-induced changes in the surface composition of lithium niobate specimens. This hypothesis is supported by the results of Auger spectroscopy and mass spectrometry researches of a LiNbO_3 single crystal in a wide temperature interval (200–1200 K)

[22]. In particular, it was shown that, at temperatures of 650–1100 K, lithium and oxygen are extracted from the bulk onto the surface of a specimen, which, as a rule, results in the formation of vacancies in the crystal. In addition, in work [15] devoted to the study of the $T_1(T)$ dependences in single and nano LiNbO_3 crystals, it was shown that, in the case of nanocrystals, the appreciable temperature dependence of the time T_1 is already observed at temperatures $T > 200$ K. But, for the polycrystal, it arises at $T > 500$ K, i.e. the hopping diffusion of lithium in nanospecimens starts at much lower temperatures. A similar result was obtained in work [23], where an increase of the lithium mobility in nanospecimens was also detected. Hence, the surface-to-volume ratio plays a considerable role in both the relaxation processes and the properties of researched objects. However, those assumptions need further researches for their verification. This is especially true for proton-exchanged specimens.

The activation energy values determined for the mobility of ${}^7\text{Li}$ nuclei cannot be related to the diffusive jumps, because they are several times lower than the corresponding values for the jumps determined in works [13–15] and manifesting themselves at temperatures higher than 500 K. The small values of energy (from 0.04 to 0.11 eV, depending on the temperature interval) and an insignificant reduction of the SLR time in the annealed specimen (see Table) could be explained either as an influence of the paramagnetic impurity or as a variation of dynamic characteristics.

The annealing of lithium niobate in vacuum is known to result in the appearance of oxygen vacancies [7]. The latter can be either neutral or positively charged, i.e. they contain either two (F-centers) or one (F^+ -centers) electron. In vicinities of such centers, the relaxation time can diminish owing to the emergence of an additional relaxation channel through the spin-spin (i.e. electron-nucleus magnetic) interaction. Since, according to our data, the SLR times in pure lithium niobate reach a value of 35 s, which coincides with the data of other authors obtained in researches of SLR in undoped LiNbO_3 , the mechanism of interaction with paramagnetic impurities is either absent or ineffective. Therefore, the low values of activation energies in the examined temperature interval are most likely associated with the tunneling of lithium ions between two neighbor positions. However, in the case of tunneling, the temper-

ature dependence of the time T_1 is absent only if the tunnel transition occurs from the ground-energy level. But if the ion is in the excited state, the coefficient of electron transmittance through the barrier (the barrier transparency) equals $D \propto \exp[(U_0 - E)/kT]$, where U_0 is the barrier height, and E is the excited-state energy at the given temperature. In our opinion, just this dependence of the coefficient D is responsible for the supposed scenario of the thermally activated process. At high temperatures (higher than 500 K), when the thermal energy kT becomes comparable with the height of the barrier for the hopping diffusion of lithium ions, the tunneling becomes a second-order mechanism and ceases to manifest itself, which was really observed in some works [13, 15]. This picture is also confirmed by the fact that the Debye temperature for lithium niobate equals $\Theta_D = 503$ K, i.e. all vibration modes can be excited above Θ_D , including the vibrations with frequencies governed by the hopping diffusion.

Hence, the appearance of F-centers after the annealing explains an insignificant reduction of the time T_1 in annealed lithium niobate (F^+ -centers, which are paramagnetic impurities, would have led to a more substantial reduction of T_1), but does not explain the substantial growth of the activation energy (see Table). Hence, the change of the activation barrier at the annealing has to be of a different origin.

Since lithium niobate was annealed in a hydrogen environment, it should be noted that, along with the emergence of F- and F^+ -centers, there may appear another structural defects. These are lithium vacancies occupied with H^+ ions, which easily form bonds with the nearest neighbors, so that the probability for lithium ions to jump to neighbor, energetically equivalent positions diminishes. The researches of NMR spectra of LiNbO_3 crystals grown up in the presence of proton donors showed that protons can occupy “rigid” positions in the crystal lattice [16, 17]. The cor-

SLR time T_1 and activation energy E_a of lithium nuclei in the initial polycrystalline lithium niobate and in the annealed one

Crystal	Initial LiNbO_3		Annealed LiNbO_3	
Temperature interval	170–300 K	350–400 K	170–300 K	350–400 K
T_1 , s	12–35	2–10	3–27	2–5
E_a , eV	0.036	0.05	0.095	0.11

responding experimental results testify to the absence of a high mobility for protons in the lithium niobate structure at temperatures close to room one. The “rigidity” of impurity proton positions in the lattice is also confirmed by our attempts to measure the NMR for H^1 , but no signal from protons was detected. This fact testifies to very large SLR times for protons owing to the “rigidity” of their positions in the lattice.

Hence, since the structural units in a lithium niobate crystal are LiO_6 and NbO_6 octahedra, it is evident that every 7Li nucleus can have three energetically equivalent positions, i.e. it can move in a three-well symmetric potential. In annealed crystals, this symmetry is broken owing to the formation of oxygen vacancies and the occupation of lithium vacancies by H^+ ions. As a result, the averaged activation energy of lithium nuclei determined from the temperature dependence of the SLR time grows by a factor of 2.6 in the low-temperature interval (170–300 K) and by a factor of 2.2 in the high-temperature one (350–430 K). Therefore, we may assert that the growth of the barrier for the lithium reorientation in the three-well potential in annealed $LiNbO_3$ is associated with its asymmetry. In other words, lithium nuclei located in the distorted zones of the annealed crystal move in an asymmetric potential. As a result, since the barrier for this motion becomes more than twice as high (see Table), the mobility of 7Li nuclei in the proton-exchanged $LiNbO_3$ decreases. Therefore, it is the slowing-down of lithium tunnel jumps between possible vacancies that enhances the optical durability of the crystal and improves the parameters of devices created on the basis of proton-exchanged niobate lithium crystals. However, this assumption needs further researches in this direction.

To summarize, while studying the temperature dependence of the SLR time T_1 in initial and annealed $LiNbO_3$, an anomaly in the relaxation behavior was found at temperatures of 300–340 K, which can be explained by a local reconstruction of the crystal lattice owing to a variation of its parameters and, probably, to a change of the surface structure in polycrystalline specimens [20, 21]. The reduction of the SLR time in the annealed crystal was shown to be related to the appearance of point defects at oxygen vacancies, with the F-centers giving the main contribution at that. The increase of the potential well depth in the annealed crystal in comparison with the undoped case

is explained by a transformation of the potential, in which lithium nuclei move, from the three-well symmetric potential to an asymmetric one, which occurs owing to the appearance of oxygen vacancies at the annealing (F-centers) and the localization of protons in the oxygen plane.

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*О.І. Овчаренко, Є.Д. Чесноков,
І.Г. Вертегел, Л.С. Іванова, Ю.П. Гнатенко*

ВПЛИВ ПРОТОНУВАННЯ НІОБАТУ
ЛІТІЮ НА МЕХАНІЗМИ ЯМР РЕЛАКСАЦІЇ ЯДЕР ${}^7\text{Li}$

Резюме

В інтервалі температур 170–430 К досліджено температурну залежність часу спин-ґраткової релаксації $T_1(T)$ ядер ${}^7\text{Li}$ в бездомішкових та протон-заміщених полікристалах LiNbO_3 . Для обох типів полікристалів виявлено аномалію

температурної поведінки T_1 в інтервалі 300–340 К, яка пояснюється локальною перебудовою ґратки. Визначені із залежності $T_1(T)$ значення енергії активації дають можливість зробити висновок про те, що домінуючим механізмом релаксації в зазначеному інтервалі температур є тунельна міграція іонів літію між вакансіями. Різниця в енергіях активації для обох полікристалів пояснюється переходом від симетричного триявного потенціалу до асиметричного внаслідок виникнення кисневих вакансій та локалізації домішкових протонів у кисневій площині.