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Dedicated to Prof. S.P. Gabuda on the occasion of his 80th birthday

SPIN-LATTICE RELAXATIONS STUDY OF WATER MOBILITY IN NATURAL NATROLITE

M. Paczwa[1], A.A. Sapiga[2], M. Olszewski[1], N.A. Sergeev[1], A.V. Sapiga[2]

[1]*Institute of Physics, University of Szczecin, Poland*
E-mail: sergeev@wmf.univ.szczecin.pl
[2]*Physical-Technical Institute, V.I. Vernadsky Crimean Federal University, Simferopol, Russia*

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The mobility of water molecules in natural natrolite ($Na_2Al_2Si_3O_{10}\cdot 2H_2O$) is investigated by the ^{1}H NMR method. The spin-lattice relaxation times in the laboratory and rotating frames (T_1 and $T_{1\rho}$) are measured as a function of the temperature for a polycrystalline sample. From experimental T_1 data it follows that at $T > 286$ K the diffusion of water molecules along channels parallel to the *c* axis is observed. From experimental $T_{1\rho}$ data it follows that at $T > 250$ K the diffusion of water molecules in transversal channels of natrolite is also observed. At a low temperature ($T < 250$ K) the dipolar interaction with paramagnetic impurities (presumably Fe^{3+} ions) becomes significant as a relaxation mechanism of ^{1}H nuclei.

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INTRODUCTION

The mineral natrolite is a typical microporous compound (zeolite) with narrow channels [1]. Careful refinements of the natrolite structure were carried out by X-ray and neutron diffraction [2—5]. The natrolite unit cell is orthorhombic with space group *Fdd*2 and contains eight formula units $Na_2Al_2Si_3O_{10}\cdot 2H_2O$. The natrolite framework consists of chains of AlO_4 and SiO_4 tetrahedra linked together via common oxygen atoms. The natrolite structure contains channels running parallel to the *c* axis (Fig. 1, *a*). Channels are connected with each other by oxygen windows (Fig. 1, *b*). These oxygen

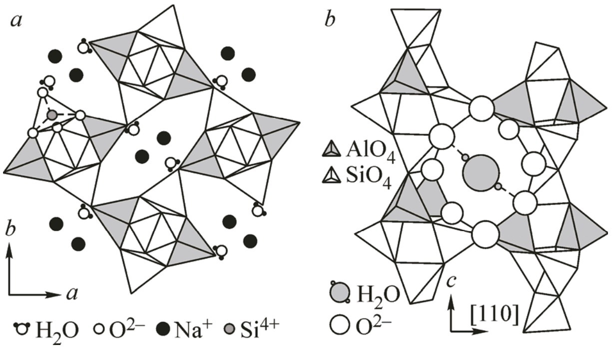

Fig. 1. Natrolite structure: projected on the (001) plane (*a*); natrolite chains and windows from oxygen ions (*b*)

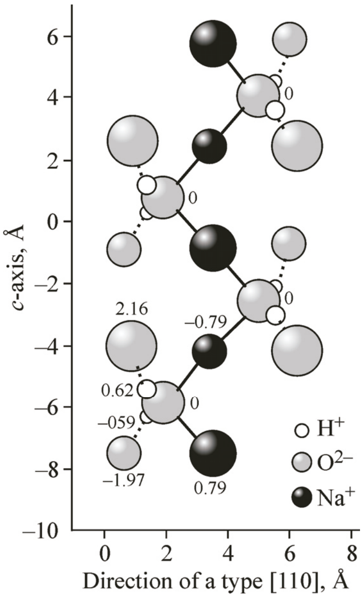

Fig. 2. Projection of the natrolite structure on the plane of water molecules. The solid lines are electrostatic bonds between water oxygen atoms and sodium ions. The dotted lines are the hydrogen bonds. The numbers specify the distance of ions above the plane

rings create a system of channels placed perpendicular to *c* axes and crossed by a framework approximately along of *a* type directions [110].

Water molecules and sodium ions form zigzag chains along the channel parallel to the *c* axis. Water molecules occupy two sites in the channels and the other sites are occupied by sodium ions. Each water molecule is coordinated by two framework oxygen atoms and by two sodium ions (Fig. 2).

One of the main features of natrolite is a narrow diameter of channels. The diameter of oxygen windows in the [110] direction is 2.60 Å, and the diameter of channel parallel to the *c* axis is only 2.08 Å [2] and it is less than 2.8 Å usually assumed for the water molecule diameter [6]. Therefore a determination of translation diffusion paths of water molecules in the natrolite channels is an interesting problem.

The mobility of water molecules in natrolite was studied by the ^{1}H NMR method in [7—14]. The first NMR research of the molecular mobility in natrolite was performed by S.P. Gabuda [7, 8]. In the pioneer paper [7] it was assumed that the main type of mobility of water molecules in natrolite at high temperatures is the diffusion along channels parallel to the *c* axis, and a water molecule jumps without breaking one of the chemical bonds of a water molecule with a sodium ion. Later in article by S.P. Gabuda from the NMR data it was expected that at a temperature above 273 K there is the diffusion of water molecules along *c* channels and at a temperature above 363 K there is also the diffusion in the perpendicular channels [8]. From the analyses of temperature transformations of the ^{1}H NMR spectra it was obtained that water molecules diffused only along the regular positions (the Schottky defects), which coincided with the positions of water molecules in a rigid lattice [10]. These results exclude the two previously proposed [6, 9] mechanisms of water mobility in natrolite: free diffusion and reorientations of water molecules around hydrogen bonds.

From our ^{23}Na and ^{27}Al NMR investigations it follows that in the temperature range up to 573 K, phase transitions in natrolite associated with modifications of the aluminosilicate framework or the structure of pores are not observed [13, 15, 16]. It also follows from these data that the diffusion of sodium cations in natrolite is absent.

In this paper we have investigated the mobility of water molecules in natrolite by pulse ^{1}H NMR, measuring the temperature dependences of the spin-lattice relaxation times in the laboratory and rotating frames.

EXPERIMENTAL

A polycrystalline sample of natural natrolite from Khibiny deposit (Kola Peninsula, Russia) was used for the NMR measurements [13]. The ^{1}H NMR spectra and spin-lattice relaxation times were measured at $\nu_0 = 400.13$ MHz frequency in a 9.4 T magnetic field using a Bruker Avance-400 NMR spectrometer. The spin-lattice relaxation time T_1 in the laboratory frame for ^{1}H nuclei was measured by the saturation-recovery method. The spin-lattice relaxation time in the rotating frame $T_{1\rho}$ was measured using the common spin-locking technique. The amplitude of the field pulse used in the $T_{1\rho}$ measurements was 14 G. The uncertainties in the determination of T_1 and $T_{1\rho}$ are about 5 % and 10 % respectively. The temperature dependences of T_1 and $T_{1\rho}$ are given in Figs. 3 and 4.

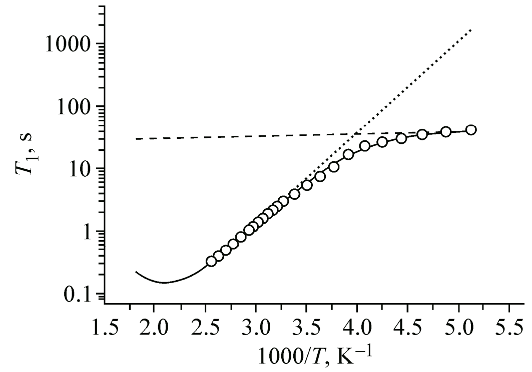

Fig. 3. Temperature dependence of the proton spin-lattice relaxation time T_1 in the laboratory frame in polycrystalline natrolite. The experimental data are illustrated by circles; the theoretical data are indicated by a straight line. The theoretical dependence of T_{1d} is indicated by a dotted line. The theoretical dependence of $T_{1\text{ne}}$ is indicated by a dashed line

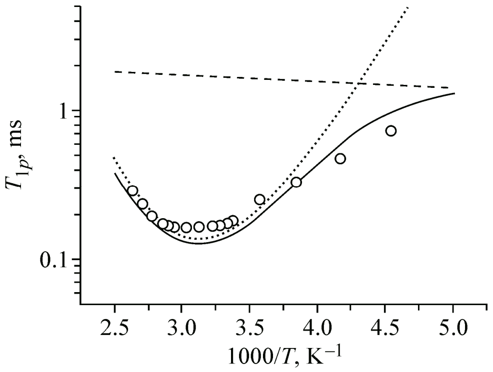

Fig. 4. Temperature dependence of the proton spin-lattice relaxation time $T_{1\rho}$ in the rotating frame in polycrystalline natrolite. The experimental data are illustrated by circles; the theoretical data are indicated by a straight line. The theoretical dependence of $T_{1\rho d}$ is indicated by a dotted line. The theoretical dependence of $T_{1\text{ne}}$ is indicated by a dashed line

RESULTS AND DISCUSSION

In the temperature regions $T > 286$ K for T_1 and $T > 250$ K for $T_{1\rho}$ the observed contributions of proton-proton interactions to T_1 and $T_{1\rho}$ are well described by the following expressions for a single dynamic process [17, 18]:

$$T_{1d}^{-1} = \frac{2}{3}\Delta M_2 \left\{ \frac{\tau_\text{c}}{1+\omega_0^2\tau_\text{c}^2} + \frac{4\tau_\text{c}}{1+4\omega_0^2\tau_\text{c}^2} \right\}, \tag{1}$$

$$T_{1\rho d}^{-1} = \Delta M_2 \left\{ \frac{\tau_\text{c}}{1+4\omega_1^2\tau_\text{c}^2} + \frac{5}{3}\frac{\tau_\text{c}}{1+\omega_0^2\tau_\text{c}^2} + \frac{2}{3}\frac{\tau_\text{c}}{1+4\omega_0^2\tau_\text{c}^2} \right\}. \tag{2}$$

Here, ω_0 and ω_1 are the Larmor frequencies associated with the static magnetic field B_0 and the radio frequency field B_1 respectively. The quantity $\Delta M_2 = M_{2\text{rl}} - M_{2\text{mav}}$ is the powder-averaged difference between the rigid lattice $M_{2\text{rl}}$ and motionally averaged $M_{2\text{mav}}$, the second moments of the proton NMR spectrum. The correlation times of the molecular motion τ_c in Eqs. (1) and (2) are assumed to follow the Arrhenius relation $\tau_\text{c} = \tau_0\exp(E_\text{a}/RT)$, where E_a is the activation energy for the appropriate process and τ_0 is a constant.

The deviation from the linear slow increase below $T = 286$ K for T_1 and $T = 250$ K for $T_{1\rho}$ is known to be caused by the interaction of nuclear spins with paramagnetic ions [17, 18]. The paramagnetic Fe^{3+} ions were observed in natrolite and investigated previously [19]. Contributions to T_1^{-1} and $T_{1\rho}^{-1}$, coming from the interaction of ^{1}H nuclear spins and unpaired electron spins of paramagnetic defects, are described by the expressions [17, 18]

$$T_{1\text{ne}}^{-1} = R_1^2 \frac{\tau_\text{ce}}{1+\omega_0^2\tau_\text{ce}^2}, \tag{3}$$

$$T_{1\rho\text{ne}}^{-1} = R_{1\rho}^2 \frac{\tau_\text{ce}}{1+\omega_1^2\tau_\text{ce}^2}, \tag{4}$$

where R_1 and $R_{1\rho}$ are the amplitudes of the fluctuating magnetic fields induced by electron-proton interactions.

It should be noted that the amplitude R_1 is determined by the components of the fluctuating magnetic fields which are perpendicular to the z axis (the z axis is parallel to $\mathbf{B}_0$, where $B_0 = \omega_0/\gamma_\text{H}$). However, the amplitude $R_{1\rho}$ is determined by the components of the fluctuating magnetic fields which are perpendicular in the rotating frame to the *x* axis (the *x* axis is parallel to $\mathbf{B}_1$, where $B_1 = \omega_1/\gamma_H$) [18].

Therefore the experimental dependences of the spin-lattice relaxation rates T_1^{-1} and $T_{1\rho}^{-1}$ in natrolite can be approximated by expressions

$$T_1^{-1} = T_{1d}^{-1} + T_{1\mathrm{ne}}^{-1}, \tag{5}$$

$$T_1^{-1} = T_{1\rho d}^{-1} + T_{1\rho \mathrm{e}}^{-1}. \tag{6}$$

The result of theoretical approximations of T_1 and $T_{1\rho}$ using expressions (5) and (6) are presented in Figs. 3 and 4.

Under calculations, we supposed that the jumps of water molecules are dynamically heterogeneous (i.e., are described by different activation energies E_a) and, correspondingly, are characterized by a normal distribution of the activation energies

$$p(E_\mathrm{a}) = \frac{1}{\sqrt{2\pi\sigma_E}} \exp\left\{ \frac{E_\mathrm{a} - \bar{E}_\mathrm{a}}{2\sigma_E^2} \right\}. \tag{7}$$

The obtained adjusting parameters are given in Table 1. From Figs. 3 and 4 one can find the satisfactory agreement between the experimental data and the calculations.

From our ^{23}Na and ^{27}Al NMR investigation of natrolite [15, 16] we obtained that the spin-lattice relaxations of ^{23}Na and ^{27}Al are governed by the electric quadrupolar interaction with the crystal electric field gradients modulated by the translation motion of H_2O molecules in natrolite pores. The activation energy for this diffusion motion is ~28 kJ/mol. From the analysis of a natrolite structure and NMR data obtained previously we concluded that this motion of water molecules is the diffusion along the *c* axis [15, 16].

The obtained temperature dependence of the proton spin-lattice relaxation time T_1 in the laboratory frame, represented in Fig. 3, confirms that in the temperature range study there is the diffusion of water molecules in natrolite along the nanochannels parallel to the *c* axis. From Fig. 3 we see that the T_1 minimum would be expected at $T \approx 500$ K, which was beyond the capability range of our apparatus.

It should be noted that it is well known that the proton spin-lattice relaxation time T_1 in the laboratory frame is sensitive to molecular motions with frequencies of about the Larmor frequency ω_0 or in the MHz region [17, 18]. However, the spin-lattice relaxation time $T_{1\rho}$ in the rotating frame is sensitive to molecular motions in the kHz region [17, 18]. The obtained temperature dependence of the proton spin-lattice relaxation $T_{1\rho}$ in the rotating frame, represented in Fig. 4, indicates that in natrolite there is the diffusion of water molecules along the nanochannels perpendicular to the *c* axis. In this case, the water molecule passes through a narrow oxygen ring of the framework (Fig. 1, *b*). Probably by this fact it can be explained that the activation energy for this diffusion process is higher than the activetion energy for the diffusion of water molecules along the nanochannels parallel to the *c* axis.

In order to explain the observed values of T_1 and $T_{1\rho}$ we theoretically calculated $M_{2\mathrm{rl}}$ and motionally averaged $M_{2\mathrm{mav}}$ second moments of the proton spectrum. For the calculation of the second moments $M_{2\mathrm{rl}}$ and $M_{2\mathrm{mav}}$ the positional parameters for all hydrogen, Al, and Na atoms were taken from the neutron diffraction study [5]. From our calculation of the intramolecular contribution (the interaction between two protons of a water molecule) to $M_{2\mathrm{rl}}$ it was found to be 23.92 G^2 (1G = 10^{-4} T) and the intermolecular contribution (the interactions between protons of different water molecules) was 0.45 G^2. The contributions to $M_{2\mathrm{rl}}$ from the proton—^{27}Al and proton—^{23}Na interactions were found to be 0.23 G^2 and 0.22 G^2, respectively. Thus, the full second moment $M_{2\mathrm{rl}}$ is 24.82 G^2. The diffusion of water molecules induces the averaging of the NMR spectrum and motionally averaged second moments $M_{2\mathrm{mav}}$ of the proton spectrum must be zero [20]. Hence, for

Table 1

Values of E_a (kJ/mol), τ_0 (s), E_el (kJ/mol), $\tau_{0\mathrm{e}}$ (s), R_1^2 (rad·kHz)^2, *and* $R_{1\rho}^2$ (rad·kHz)^2 *obtained from* T_1 *and* $T_{1\rho}$

	E_a	τ_0	E_el	$\tau_{0\mathrm{e}}$	R_1^2, $R_{1\rho}^2$
T_1	28	$2\cdot10^{-13}$	0.84	$1.7\cdot10^{-9}$	450
$T_{1\rho}$	37.3	10^{-12}	0.84	$5\cdot10^{-12}$	$8.5\cdot10^{7}$

the diffusion process in Eq. (1) we must use $\Delta M_2 = M_{2\mathrm{rl}}$. The minimum in the temperature dependence of T_1 is observed when $\omega_0\tau_c \approx 1$ in Eq. (1) [17, 18]. Therefore we have that at the minimum in the temperature dependence of T_1 the spin-lattice relaxation time in the laboratory frame is expected to be

$$(T_{1d})_{\min} \approx \frac{3\omega_0}{M_{2\mathrm{rl}}} \approx 0.4s. \tag{8}$$

This value of $(T_{1d})_{\min}$ is close to the expected minimum value of the spin-lattice relaxation time in the laboratory frame which would be expected at $T \approx 500$ K (Fig. 3)

It should be noted that Thompson et al. [9] assumed that the temperature dependence of T_1 in natrolite is related to 180° flip motions of water molecules. From our calculations for this model of the water molecules dynamics in natrolite it follows that $\Delta M_2 = M_{2\mathrm{rl}} - M_{2\mathrm{mav}} \approx 0.86\ \mathrm{G}^2$ and the minimum in the temperature dependence of T_1 the spin-lattice relaxation time in the laboratory frame is expected to be

$$(T_{1d})_{\min} \approx \frac{3\omega_0}{\Delta M_2} \approx 26s. \tag{9}$$

This value of $(T_{1d})_{\min}$ greatly exceeds the expected minimum value of the spin-lattice relaxation time in the laboratory frame which would be expected at $T \approx 500$ K (Fig. 3). Consequently, from our considerations it follows that at $T > 286$ K the diffusion of water molecules along the channels parallel to the *c* axis is responsible for the spin-lattice relaxation time T_1 of ^{1}H nuclei in natrolite.

From Fig. 4 and data presented in Table 1 it follows that in natrolite there is another dynamic process for water molecules. For this dynamic process, the activation energy is higher than the activation energy for the diffusion of water molecules along the nanochannels parallel to the *c* axis.

From Eq. (2) we have that the minimum in the temperature dependence of T_1 is observed when $\omega_1\tau_c \approx 1$ in Eq. (2) [17, 18]. Therefore we have that at the minimum in the temperature dependence of $T_{1\rho}$ the spin-lattice relaxation time in the rotating frame is expected to be

$$(T_{1\rho})_{\min} \approx \frac{5\omega_0}{M_{2\mathrm{rl}}} \approx 0.1ms. \tag{10}$$

The obtained value of $(T_{1\rho d})_{\min}$ coincides very well with the experimentally measured value. From the analysis of the natrolite structure and the NMR data obtained previously we concluded that this motion of water molecules is the diffusion along the nanochannels perpendicular to the *c* axis.

CONCLUSIONS

By measuring the ^{1}H spin-lattice relaxation time T_1 in the laboratory frame for a polycrystalline sample of natrolite as functions of the temperature we have established that at $T > 286$ K the diffusion of water molecules along the nanochannels parallel to the *c* axis is responsible for the spin-lattice relaxation in the laboratory frame. The activation energy of this motion is ~28 kJ/mol. By measuring the ^{1}H spin-lattice relaxation time $T_{1\rho}$ in the rotating frame for a polycrystalline sample of natrolite as functions of the temperature we have established that at $T > 250$ K the diffusion of water molecules along the nanochannels perpendicular to the *c* axis is responsible for the spin-lattice relaxation in the rotating frame. The activation energy of this motion is ~37.3 kJ/mol. The dipolar interactions with paramagnetic impurities (presumably with Fe^{3+} ions) become significant as a relaxation mechanism of the ^{1}H nuclei only at a temperature < 250 K.

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REFERENCES

1. *Engelhardt G., Michel D.* High-Resolution Solid-State NMR of Silicates and Zeolites. – Chichester, New York, Brisbane, Toronto, Singapore: John Wiley&Sons, 1987.
2. *Meier W.M.* // Z. Kristallogr. – 1960. – **113**. – P. 430.
3. *Torrie B.H., Brown I.D., Petch H.E.* // Can. J. Phys. – 1964. – **42**. – P. 229.

4. *Pechar F., Schafer W., Will G.* // Z. Kristallog. – 1983. – **164**. – P. 19.
5. *Artioli G., Smith J.V., Kvick A.* // Acta. Crystallogr. – 1984. – **40**. – P. 1658.
6. *Breck D.W.* Zeolite molecular sieves. – New York, London, 1974.
7. *Gabuda S.P.* // Dokl. Akad. Nauk SSSR. – 1962. – **146**. – N 4. – P. 840.
8. *Belitskii I.A., Gabuda S.P.* // Chem. Erde. – 1968. – **B27**. – P. 79.
9. *Thompson R.T., Knispel R.R., Petch H.E.* // Can. J. Phys. – 1974. – **52**. – P. 2164.
10. *Sapiga A.V., Sergeev N.A., Shcherbakov V.N., Gabuda S.P.* // J. Struct. Chem. – 1986. – **27**. – P. 183.
11. *Sapiga A.V., Sergeev N.A.* // Mol. Phys. Rep. (Poland). – 2000. – **29**. – P. 60.
12. *Sapiga A.V., Sergeev N.A.* // Mol. Phys. Rep. (Poland). – 2001. – **34**. – N 2. – P. 137.
13. *Sapiga A.V., Sergeev N.A.* // Cryst. Res. Technol. – 2001. – **8-10**. – P. 875.
14. *Olszewski M., Sergeev N.A., Sapiga A.V.* // Z. Naturforsch. – 2004. – **A59**. – P. 501.
15. *Paczwa M., Sapiga A.A., Olszewski M., Sergeev N.A., Sapiga A.V.* // Appl. Magn. Reson. – 2015. – **46**. – P. 583.
16. *Paczwa M., Sapiga A.A., Olszewski M., Sergeev N.A., Sapiga A.V.* // Z. Naturforsch. – 2015. – **A70**. – P. 295.
17. *Abragam A.* The Principles of Nuclear Magnetism. – Oxford, 1961.
18. *Slichter Ch.P.* Principles of Magnetic Resonance. – Berlin: Springer, 2010.
19. *Vinokurov V.M., Gaite J.M., Bulka G.R., Khasanova N.M., Nizamutdinov N.M., Galeev A.A., Rudowicz C.* // J. Magn. Reson. – 2002. – **155**. – P. 57.
20. *Sergeev N.A., Falaleev O.V., Gabuda S.P.* // Sov. Phys. Solid State. – 1969. – **11**. – P. 2248.