

Dynamic of water molecules in natrolite

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Molecular mobility of water molecules has been investigated in the natural zeolite natrolite ($Na_2Al_2Si_3O_{10} \cdot 2H_2O$) by 1H NMR. Spin-lattice relaxation times in the laboratory and rotating frames (T_1 and $T_{1\rho}$) have been measured as a function of temperature for a polycrystalline sample. It has been shown that the spin-lattice relaxations times of 1H are governed by the translation motions of water molecules in the natrolite pores. 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 observed also. At low temperature ($T < 250$ K) the dipolar interaction with paramagnetic impurities (presumably with Fe^{3+} ions) become significant as a relaxation mechanism of 1H nuclei.

Keywords: Zeolite, NMR, natrolite, water mobility

I. INTRODUCTION

The mineral natrolite ($Na_2Al_2Si_3O_{10} \cdot 2H_2O$) is the typical channel-type compound with porous structure (zeolite) [1]. The natrolite unit cell is orthorhombic with space group $Fdd2$ and contains eight formula units [2-5]. The natrolite framework consists of chains from AlO_4 and SiO_4 tetrahedral linked together via common oxygen atoms. In the natrolite structure there are two type of channel which are perpendicular and parallel to the c -axis. The sodium ions and water molecules are located into these channels and the other sites are occupied by sodium ions. Each sodium ion is coordinated by four framework's oxygen atoms and by two water molecules (Fig.1).

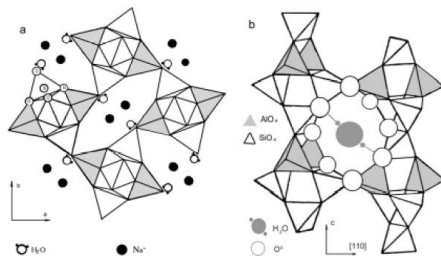


FIG. 1. The natrolite structure. (a) Projected on (001) plane. (b) The natrolite chains and "window" from oxygen ions.

It is well known that nuclear magnetic resonance (NMR) allows to obtain direct information about the crystal structure and internal mobility in one [6,7]. NMR of 1H in natrolite was studied in [8-16]. From NMR data it follows that water molecules diffuse along the vacancies whose positions coincide with regular position of water molecules in crystal structure of natrolite (Fig.2). This motion is the "hopping" motion, i.e. the water molecules spend most of their time in a potential well corresponding to equilibrium positions, and only a very small fraction moves between these potential wells. Thompson et al. [10] assumed that the 180° flip motion of the water molecules take place in natrolite. However using only method of the proton

magnetic resonance it is difficult to detect this kind of water molecular motion. From our investigation [15] it was obtained

that for the temperatures higher than 290 K the diffusion water molecules along the c -axis is observed (Fig.2). From the analysis of a natrolite structure and NMR data we concluded that the 180° flip motion of water molecules take place simultaneously with their diffusion along the c -axis. If a temperature is higher than 250 K water molecules diffuse in channels of perpendicular to c -axis [15].

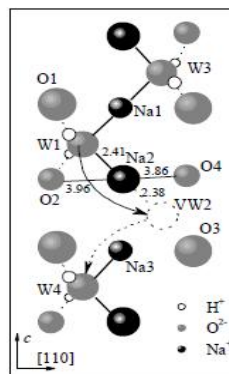


FIG. 2. The vacancy mechanism of water diffusion in natrolite.

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

II. EXPERIMENTAL PART

A polycrystalline sample of natural natrolite from Khibiny deposit (Kola Peninsula, Russia) was used for the NMR measurements [14]. The 1H NMR spectra and spin-lattice relaxation times were measured at $\nu_0 = 400.13$ MHz frequency in 9.4 T magnetic field using a Bruker Avance-400 NMR spectrometer. The spin-lattice relaxation time T_1 in the

laboratory frame for ^1H nuclei was measured by 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 $T_{1\rho}$ measurements was 14 G. The uncertainty in the determination of T_1 and $T_{1\rho}$ are about 5% and 10% respectively. The temperature dependences of the T_1 and $T_{1\rho}$ are given in Fig.3 and Fig.4.

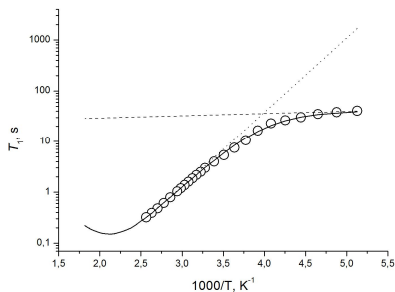


FIG. 3. Temperature dependence of the proton spin-lattice relaxation time, T_1 , in the laboratory frame in polycrystalline natrolite. The experimental data are illustrated by circles; the theoretical data are indicated by a straight line. The theoretical dependence of T_{1id} is indicated by a dotted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

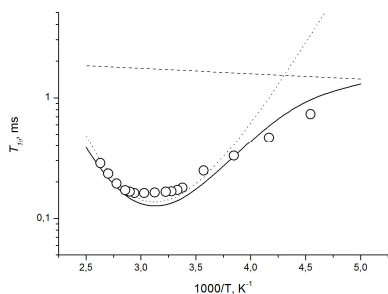


FIG. 4. Temperature dependence of the proton spin-lattice relaxation time, $T_{1\rho}$, in the rotating frame in polycrystalline natrolite. The experimental data are illustrated by circles; the theoretical data are indicated by a straight line. The theoretical dependence of T_{1pd} is indicated by a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

III. ANALYSIS OF THE RELAXATION DATA

In the temperature regions $T > 286\text{ K}$ for T_1 and $T > 250\text{ K}$ for $T_{1\rho}$ the observed contributions of proton-proton interactions to the T_1 and $T_{1\rho}$ are well described by the following expressions for a single dynamical processes [6,7]

$$T_{1d}^{-1} = \frac{2}{3} \Delta M_2 \left\{ \frac{\tau_c}{1 + \omega_0^2 \tau_c^2} + \frac{4\tau_c}{1 + 4\omega_0^2 \tau_c^2} \right\}, \quad (1)$$

$$T_{1pd}^{-1} = \Delta M_2 \left\{ \frac{\tau_c}{1 + 4\omega_1^2 \tau_c^2} + \frac{5}{3} \frac{\tau_c}{1 + \omega_0^2 \tau_c^2} + \frac{2}{3} \frac{\tau_c}{1 + 4\omega_0^2 \tau_c^2} \right\}. \quad (2)$$

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 $\Delta M_2 = M_{2rl} - M_{2mav}$ is the powder-averaged difference between the rigid lattice, M_{2rl} , and motionally averaged, M_{2mav} , second moments of the proton NMR spectrum. The correlation times of the molecular motion, τ_c , in Eq.(1) and Eq.(2) are assumed to follow the Arrhenius relation $\tau_c = \tau_0 \exp(E_a/RT)$, where E_a is the activation energy for the appropriate process and τ_0 a constant.

The deviation from linear slowly increasing below $T = 286\text{ K}$ for T_1 and $T = 250\text{ K}$ for $T_{1\rho}$ is known to be caused by the interaction of nuclear spins with paramagnetic ions [6,7]. The paramagnetic ions Fe^{3+} were observed in natrolite and investigated earlier [17]. Contribution to T_1^{-1} and $T_{1\rho}^{-1}$, coming from the interaction of ^1H nuclear spins and unpaired electron spins of paramagnetic defects are described by the expressions [6,7]

$$T_{1ne}^{-1} = R_1^2 \frac{\tau_{ce}}{1 + \omega_0^2 \tau_{ce}^2}, \quad (3)$$

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

where R_1 and $R_{1\rho}$ are the amplitudes of the fluctuating magnetic fields that induced by the 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 z-axis (z-axis is parallel to \mathbf{B}_0 , where $\mathbf{B}_0 = \omega_0 / \gamma_{\text{H}}$). However the amplitude $R_{1\rho}$ is determined by the components of the fluctuating magnetic fields which are perpendicular in the rotating frame to x-axis (x-axis is parallel to \mathbf{B}_1 , where $\mathbf{B}_1 = \omega_1 / \gamma_{\text{H}}$) [6,7].

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

$$T_1^{-1} = T_{1d}^{-1} + T_{1ne}^{-1}, \quad (5)$$

$$T_{1\rho}^{-1} = T_{1pd}^{-1} + T_{1\rho ne}^{-1}. \quad (6)$$

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

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

$$p(E_a) = \frac{1}{\sqrt{2\pi\sigma_E}} \exp\left\{ -\frac{E_a - \bar{E}_a}{2\sigma_E^2} \right\}, \quad (7)$$

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

Table. Values of E_a (kJ/mol), τ_0 (s), E_{aj} (kJ/mol), τ_{0e} (s), R_1^2 ($\text{rad}\cdot\text{kHz}^2$) and $R_{1\rho}^2$ ($\text{rad}\cdot\text{kHz}^2$) obtained from T_1 and $T_{1\rho}$

	E_a	τ_0	E_{aj}	τ_{0e}	$R_1^2, R_{1\rho}^2$
T_1	28	$2 \cdot 10^{-13}$	0.84	$1.7 \cdot 10^{-9}$	450
$T_{1\rho}$	37.3	10^{-12}	0.84	$5 \cdot 10^{-12}$	$8.5 \cdot 10^7$

Early from our ^{23}Na and ^{27}Al NMR investigation of natrolite [18,19] 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 translation motion of H_2O molecules in the natrolite pores. The activation energy for this diffusion motion is $\sim 28\text{ kJ/mol}$. From the analysis of a natrolite structure and NMR data obtained early we concluded that this motion of water molecules is the diffusion along the c-axis [18,19].

The obtained temperature dependence of the proton spin-lattice relaxation time, T_1 , in the laboratory frame, represented in Fig.3, confirms that in natrolite in the temperature range study there is the diffusion of water molecules 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 the our apparatus.

It should be noted that it is well known that the proton spin-lattice relaxation time, T_1 , in laboratory frame is sensitive to molecular motions with frequencies order Larmor frequency ω_0 or in the MHz region [6,7]. However the spin-lattice relaxation time $T_{1\rho}$ in the rotating frame is sensitive to molecular motion in the kHz region [6,7]. 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 and the activation energy for this diffusion process is high than the activation energy for the diffusion of water molecules along the nanochannels parallel to the c axis. This result coincides with results obtained in [15].

In order to explain the observed values of T_1 and $T_{1\rho}$ we theoretically calculated M_{2nl} , and motionally averaged, M_{2max} , second moments of the proton spectrum. For the calculation of the second moments M_{2nl} and M_{2max} 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 water molecule) to M_{2nl} was founded to be $23.92 G^2$ ($1 G = 10^{-4} T$) and the intermolecular contribution (the interactions between protons of different water molecules) was equal to $0.45 G^2$. The contributions to M_{2nl} from the interactions proton - ^{27}Al and proton - ^{23}Na were founded to be $0.23 G^2$ and $0.22 G^2$, accordingly. So the full second moment M_{2nl} is equal $24.82 G^2$. The diffusion of the water molecules induces the averaging of NMR spectrum and motionally averaged, M_{2max} , second moments of the proton spectrum must be equal zero [20, 21]. So for the diffusion process in Eq.(1) we must to use $\Delta M_2 = M_{2nl}$. The minimum in the temperature dependence of T_1 is observed when $\omega_0 \tau_c \approx 1$ in Eq.(1) [6,7]. Therefore we have that at the minimum in the temperature dependence of T_1 the spin-lattice relaxation time in the laboratory frame would be expected to equal

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

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

In the introduction it should be noted that Thompson et al. [10] assumed that the temperature dependence of T_1 in natrolite is connected with the 180° flip motions of the water molecules. For this model of the water molecules dynamic in natrolite it is follows from our calculations that $\Delta M_2 = M_{2nl} - M_{2max} \approx 0.86 G^2$ and the minimum in the temperature dependence of T_1 the spin-lattice relaxation time in the laboratory frame would be expected to equal

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

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

From Fig.4 and data represented in Table, it follows that in natrolite there is other dynamical process for the water

molecules. For this dynamical process the activation energy is high 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 $\omega_0 \tau_c \approx 1$ in Eq.(2) [6,7]. Therefore we have that at the minimum in the temperature dependence of $T_{1\rho}$ the spin-lattice relaxation time in the rotating frame would be expected to equal

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

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

IV. CONCLUSION

By measuring the 1H spin-lattice relaxation time, T_1 in the laboratory frame for a polycrystalline sample of natrolite as functions of temperature, we have established that at $T > 286$ K the diffusion of water molecules along the nanochannels parallel to 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 1H spin-lattice relaxation time, $T_{1\rho}$ in the rotating frame for a polycrystalline sample of natrolite as functions of temperature, we have established that at $T > 250$ K the diffusion of water molecules along the nanochannels perpendicular to 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 1H nuclei only at temperature < 250 K.

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