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NMR Investigation of Natrolite Structure

The temperature dependencies of NMR spectra of ^{1}H, ^{23}Na and ^{27}Al nuclei in natrolite $Na_2Al_2Si_3O_{10}$ $2H_2O$ have been studied. It has been shown that the model of the normal distribution of the activation energy may be considered as a preferable model for the diffusion of the water molecules in the natrolite. The influence of the water molecule diffusion on the NMR spectra of ^{23}Na and ^{27}Al has been discussed. It has been established that the internal mobility of aluminium and sodium ions does not occur in natrolite.

Keywords: crystal structure, Nuclear Magnetic Resonance (NMR), natrolite, diffusion, zeolites

1. Introduction

The mineral natrolite ($Na_2Al_2Si_3O_{10}$ $2H_2O$) is the typical channel-type compound with porous structure (zeolite). The unit cell of this mineral is orthorhombic with space group Fdd2 and contains eight formula units (MEIER; PECHAR et. al.; TORRIE et. al.; ARTIOLI et. al.). The natrolite framework consists of chains AlO_4 and SiO_4 tetrahedra linked together via common oxygen atoms. The sodium ions and water molecules are located into channels running both perpendicular and parallel to the **c** axis. Water molecules occupy two sites in the 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.

It is well known, that Nuclear Magnetic Resonance (NMR) method allows obtaining direct information about the crystal structure and internal mobility in one. Several investigators (GABUDA 1962; GABUDA et. al. 1963; SHCHERBAKOV 1972; SAPIGA et. al. 1986, 1998, 2000, THOMPSON et. al.) have studied the ^{1}H NMR in natrolite. It has been established that there are two different kinds of the water molecular motion. The molecular motion of the first kind is the 180^0 flip motion and second one is the diffusion of the water molecules. From NMR data it follows that water molecules diffuse along the vacancies whose positions coincide with the regular positions of water molecules (SAPIGA et. al. 1986). The chemical and structurally equivalence of water molecules suggests that the diffusive jumps of water molecules may be characterised by the same correlation time τ_c. However, this suggestion does not agree to observed temperature transformations of the NMR spectra (SAPIGA et. al. 1998, 2000).

The NMR studies of ^{27}Al and ^{23}Na nuclei in natrolite at room temperature have been reported by several investigators (PETCH et. al.; GABUDA et. al. 1973; SHCHERBAKOV 1972; SHCHERBAKOV et. al. 1981). From NMR spectra of ^{27}Al and ^{23}Na nuclei the quadrupolar coupling constants and parameters asymmetry of electric field gradient tensors of these nuclei have been determined.

In the present paper, the temperature dependencies of NMR spectra of ^{1}H, ^{23}Na, ^{27}Al have been studied to obtain information about the motions of the water molecules, sodium and aluminium ions in natrolite.

2. Results and discussion

The natrolite crystalline and polycrystalline samples from the Khibiny deposit (Kola Peninsula, Russia) were used in this study. The chemical analysis of the natrolite sample [(Na$_2$O)(Al$_2$O$_3$) 3(SiO$_2$) 2H$_2$O] yielded the following composition: SiO$_2$ - 46.45 %; Al$_2$O$_3$ - 27.1 %; Na$_2$O – 15.15 %. The water H$_2$O content determined by thermogravimetry method was 9.52 %. In sample there are small contents ($\approx$ 0.02 %) of CaO, K$_2$O, SrO and Fe$_2$O$_3$. A clear single crystal of natrolite 5 mm×6 mm×10mm in size was used. The orientation of the crystal was carried out on the basis of X-ray diffraction data.

The ^{23}Na and ^{27}Al NMR spectra in natrolite were obtained with an 11 MHz oscillator on single crystals and polycrystalline samples. The ^{1}H NMR spectra were obtained with a 30 MHz NMR spectrometer on single crystals at various crystal orientations in external magnetic field ($\mathbf{B}_0$). The sample has been heated in the probe of NMR spectrometer by a blowing of hot air.

2.1. The NMR spectra of ^{1}H

The experimental temperature dependencies of the second moment M$_2$ and the shape of the NMR spectrum for the case when the vector of the magnetic field $\mathbf{B}_0$ lies in [110] direction are given in Fig. 1 and Fig. 2b.
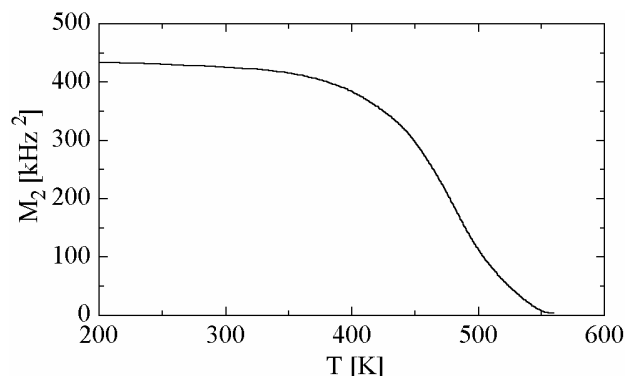

Fig. 1: The temperature dependence of the ^{1}H NMR second moment for the case when vector $\mathbf{B}_0$ lies in [110] direction.

One can see from Fig. 1 that the second moment of ^{1}H NMR spectrum does not depend on the temperature below 250 K. From this fact it follows that the internal mobility of water molecules is absent in this temperature region. The internal mobility of the water molecules is observed at T > 250 K. The decreasing of the second moment to practically a zero value indicates that internal mobility of the water molecules is the diffusion.

Theoretical NMR spectrum for the case when vector $\mathbf{B}_0$ is parallel to [110] direction contains two Pake's doublets with splitting $\Delta\nu_1$ = - 43 kHz and $\Delta\nu_2$ = 38 kHz (SAPIGA et. al. 1986). At room temperature the intermolecular dipolar interactions between magnetic moments of the water protons lead to the broadening of the doublet lines and the observed NMR spectrum consists of the nonresolved doublets. The heating of the crystal induces the motional average of the intramolecular and intermolecular dipolar H-H interactions and at

the high temperature the single narrow doublet is observed (Fig. 2a.5). The value of the splitting of this doublet coincides with the average value $(\Delta\nu_2 + \Delta\nu_1)/2$ (SAPIGA et. al. 1986). This fact indicates that the water molecules diffuse along the Schottky defects.

In order to explain the observed temperature transformations of the ^{1}H NMR spectra we have assumed that the diffusion jumps of water molecules may be characterised by the same correlation time τ_c. The theoretical temperature dependence of the NMR spectrum, obtained by the spin density matrix (KAPLAN et. al.; SERGEEV et. al.), is shown in Fig. 2a.

Fig. 2: The temperature dependence of the ^{1}H NMR spectrum of natrolite for the case when vector **B**$_0$ lies in [110] direction: (a) theoretical NMR spectra obtained for the model of homogeneous diffusion of water molecules with the activation energy E_a = 73 kJ/mole; (b) experimental NMR spectra; (c) theoretical NMR spectra obtained for the normal distribution of the activation energy (E_a = 73 kJ/mole and σ_E = 4.2 kJ/mole).
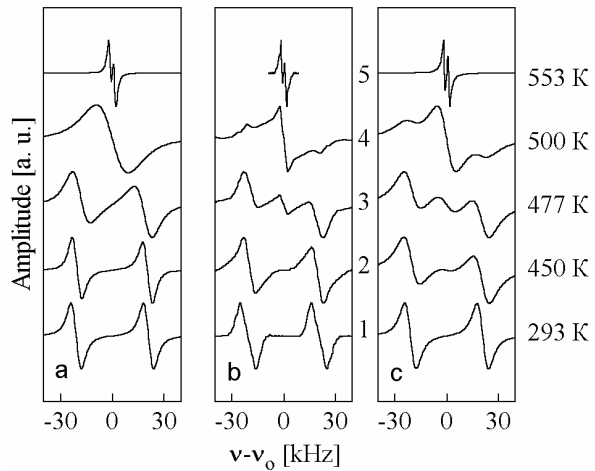
These spectra have been obtained assuming that τ_c fulfils an Arrhenius activation law

$$\tau_c = \tau_0 \exp\left(\frac{E_a}{RT}\right). \tag{1}$$

From comparison of the experimental and theoretical NMR spectra it follows that the model of the water molecules diffusion with single correlation time τ_c is not in agreement with the experiment. The existence of the additional spectral lines in the central part of NMR spectra (Fig. 2b.3,4) may be explained only assuming that there is a dynamic heterogeneity of the water molecules.

We calculated also the theoretical temperature dependencies of NMR spectra in assumption that there are two kinds of water molecules with the activation energies E_{a1} = 72 kJ/mole and E_{a2} = 76 kJ/mole, respectively. The agreement between the experimental data and the fitted NMR spectra was good over the whole temperature range. However, we suggest that the model of two activation energies for the diffusion of the water molecules in natrolite is not reasonable and hardly explainable.

There is plenty of evidence in the literature (RESING; PRIVALOV et al.) to suggest that the molecular diffusion in solids is not characterised by the single correlation time. We assumed that a distribution of the correlation times τ_c is due to a distribution of the activation energy E_a and the distribution function of E_a is the normal distribution

$$f(E_a) = A \exp\left[-\frac{1}{2}\left(\frac{E_a - \overline{E}_a}{s_E}\right)^2\right]. \tag{2}$$

It is well known that a normal distribution of E_a leads to the lognormal distribution of the correlation time τ_c (RESING).

The theoretical NMR spectra obtained for the case of the normal distribution of the activation energy E_a are shown in Fig. 2c. From good agreement between the experimental and simulated NMR spectra it can be concluded that the model of the normal distribution of the activation energy may be considered as a preferable model for the diffusion of the water molecules in the natrolite. It is reasonable to expect that the distribution of the activation energy for diffusion of the water molecules must be connected with structural and dynamic peculiarities of the zigzag chains in the natrolite pores formed from the water molecules and sodium ions. The vacancy of the water molecule must lead to local distortion of the oxygen polyhedron coordinating the sodium ion (Fig. 3).
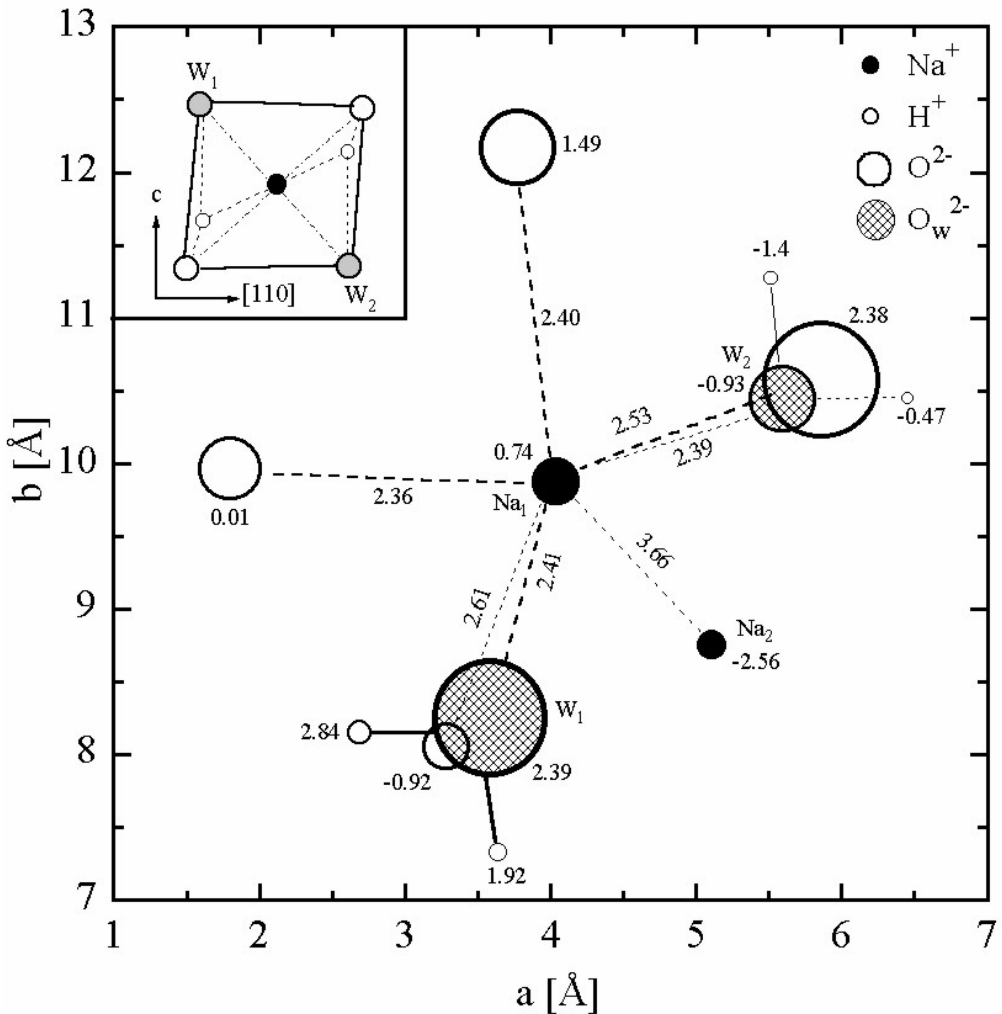

Fig. 3: The projection of the natrolite structure fragment on the (001) plane. Inset: The projection of this fragment on the (110) plane.

This distortion will also distort the neighbouring oxygen polyhedrons and will lead to the distribution of the activation energy for diffusion of the water molecules. It should be noted that such microscopic defect can also "attract" of the H_2O vacancies and it leads to non-homogeneous distribution of the water molecule vacancies in the crystal structure (BELASHCHENKO; PRIVALOV et al.).

2.2. The NMR spectra of ^{27}Al and ^{23}Na

The experimental results of the quadrupolar coupling constant (e^2qQ/h) and the asymmetry parameter (η) of electric field gradient (EFG) tensors for ^{27}Al and ^{23}Na nuclei as a function of the temperature obtained for the polycrystalline natrolite sample are shown in Figs. 4 and 5, respectively.

One can see from Fig. 4 that the quadrupolar coupling constant (QCC) of ^{27}Al nuclei does not practically depend on the temperature for T < 450 K. In the temperature region of 450 K < T < 600 K the gradual decreasing of the quadrupolar coupling constant is observed. From this fact it follows that the intensive internal mobility of aluminium ions is absent in this temperature region.
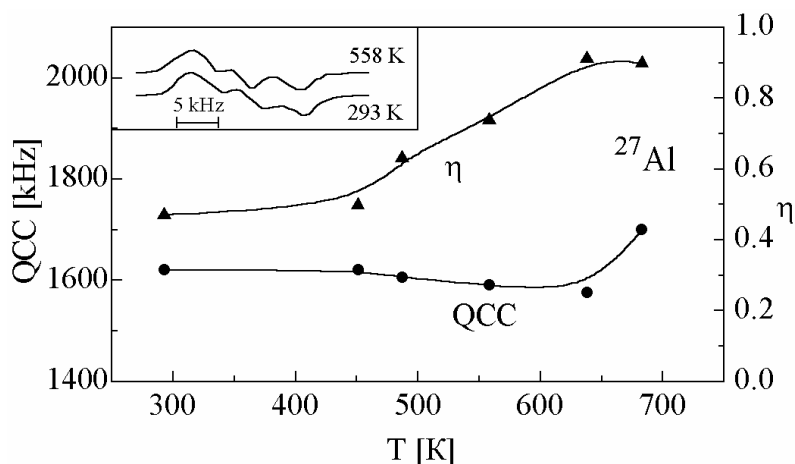

Fig. 4: The temperature dependencies of the ^{27}Al quadrupolar coupling constant (QCC) and the asymmetry parameter η in the polycrystalline natrolite. Inset: NMR spectra of ^{27}Al at different temperatures.

At T > 620 K the quadrupolar coupling interaction of ^{27}Al is increased. This increasing of the quadrupolar coupling constant of ^{27}Al nuclei at T > 620 K is probably connected with the complete dehydration of natrolite. It is known that in the temperature region of 520 K < T < 620 K there is a complete dehydration of natrolite and at T > 620 K the natrolite transforms in a waterless modification known as a metanatrolite (ALBERTI et al.; FANG). The space group of the metanatrolite unit cell is F2 and so the dehydration of natrolite must lead to a distortion of the aluminosilicate framework and to the increasing of the electric field gradient at the ^{27}Al sites. The small decreasing of the quadrupolar coupling constant at T < 620 K is probably connected with the intensive diffusion of the water molecules and partial dehydration of natrolite in this temperature range. It is interesting to note that the intensive diffusion of the water molecules and the partial dehydration of natrolite induce small changes in ^{27}Al NMR spectra. From this fact it follows that the contribution of the electric dipolar moments of the water molecules into electric field gradient at the occupation site of

aluminium is small. Using the simple model of the point electric charges, we calculated the main component of the electric field gradient tensor at the aluminium position (Table 1) taking into consideration ions of the whole lattice and the lattice without water molecules. From our theoretical calculation it follows that contribution of the dipolar moments of the water molecules into the [27]Al quadrupolar coupling constant is less then few percent. This result is not surprising because the aluminium ions are sited in aluminosilicate framework and water molecules are sited far from them. The observed temperature dependence of the asymmetry parameter η (Fig. 4) is probably connected with the turning of the aluminosilicate tetrahedrons on an angle approximately 11^0 at dehydration of natrolite (Alberti et al.).
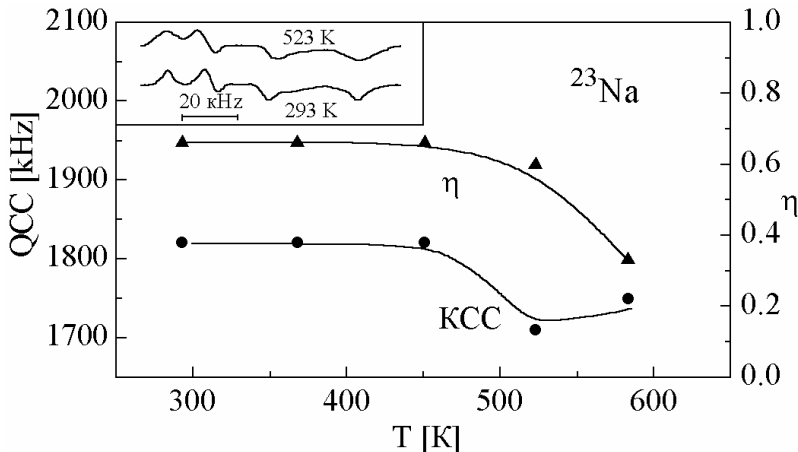

Fig. 5: The temperature dependencies of the [23]Na quadrupolar coupling constant (QCC) and the asymmetry parameter η in the polycrystalline natrolite. Inset: NMR spectra of [23]Na at different temperatures.

From Fig. 5 it follows that the quadrupolar coupling constant and the asymmetry parameter of [23]Na nuclei do not depend on the temperature in the region of T < 450 K. The quadrupolar coupling constant is decreased at T > 450 K. The asymmetry parameter is decreased at T > 500 K. Because of the positions of [23]Na ions in zeolite pores, the observed decreasing of the quadrupolar interaction constant and the asymmetry parameter of [23]Na nuclei may be accounted for by diffusion of water molecules or by translational diffusion of Na ions in the natrolite channels. In order to separate the contributions of these two possible diffusion mechanisms in NMR spectra of ^{23}Na, we investigated the NMR of [23]Na in the natrolite single crystal. In natrolite there are two structurally nonequivalent [23]Na nuclei and the well-resolved fine structure of NMR spectra caused by the second-order quadrupolar effects is observed at some orientations of crystal in external magnetic field $\mathbf{B}_0$ (Shcherbakov 1972). The experimental temperature dependencies of the quadrupolar second-order shifts of the central NMR lines of the two structurally nonequivalent [23]Na nuclei, for the case when the vector of the magnetic field $\mathbf{B}_0$ is parallel to [110] direction, are shown in Fig. 6. The intensive diffusion of [23]Na ions in natrolite pores must lead to the magnetically equivalency of [23]Na nuclei and to the averaging of the second-order quadrupolar shifts of different [23]Na nuclei. In reality, such an effect is not observed (Fig. 6). From the observed above temperature dependency of the second-order quadrupolar shifts of the two structurally nonequivalent [23]Na nuclei at $\mathbf{B}_0 \parallel$ [110] it follows that the observed earlier decreasing of the quadrupolar interaction constant and the asymmetry parameter of [23]Na nuclei in polycrystalline natrolite are probably connected with the diffusion of water molecules. Using the simple model of the

point electric charges, we calculated the components of the electric field gradient tensor at the position of sodium ion (Table 1). In the natrolite channel the sodium ion is surrounded by six oxygen ions (Fig. 3). Four oxygen ions are the oxygen ions of a framework and the other oxygen ions are the oxygen of water molecules. Six oxygen ions form a distorted polyhedron (Fig. 3).
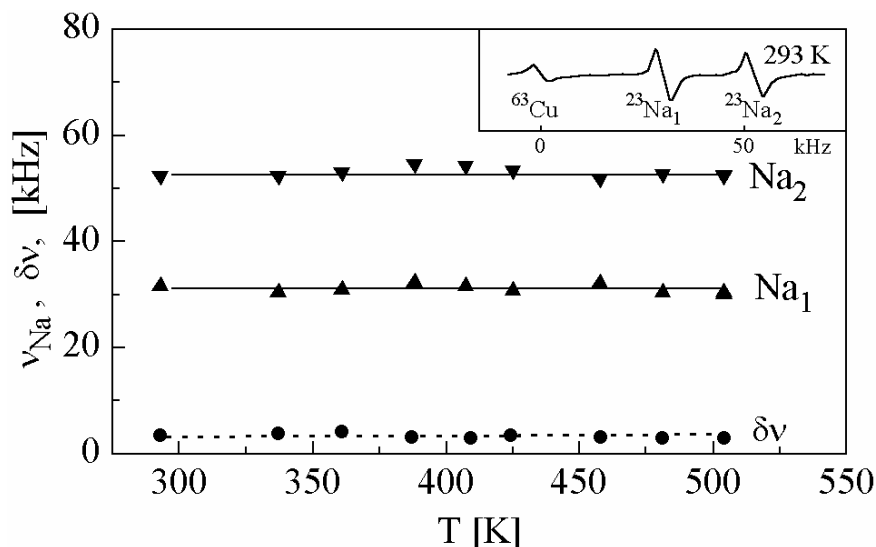

Fig. 6: The temperature dependencies of the second-order quadrupolar shifts and the linewidth ($\delta\nu$) of ^{23}Na NMR spectra for the two structurally nonequivalent ^{23}Na ions in the natrolite single crystal. The vector of the magnetic field $\mathbf{B}_0$ is parallel to [110] direction. Inset: the central part of NMR spectrum of ^{23}Na in a single crystal.

Tab. 1: The theoretical values of main component of the EFG tensor (eq) at the positions of aluminium and sodium ions in a natrolite (in units 10^{20} V/m)

Nucleus	(eq)				
	A*)	B*)	C*)	D*)	E*)
^{23}Na	-1.11	2.64	1.50	1.47	2.52
^{27}Al	3.45	3.48	-	-	-

A*) – the value (eq) calculated using the electric charges of the ions of the whole lattice; B*) - the value (eq) calculated using the electric charges of the ions of the whole lattice minus the electric charges of all water molecules; C*)- the value (eq) calculated using the electric charges of the ions of the whole lattice minus the electric charges of the water molecule W_1 (Fig. 3); D*)- the value (eq) calculated using the electric charges of the ions of the whole lattice minus the electric charges of the water molecule W_2 (Fig. 3); E*)- the value (eq) calculated using the electric charges of the ions of the whole lattice minus the electric charges of the water molecules W_1 and W_2 (Fig. 3).

Using for the sodium ion the Sternheimer antishielding factor $\gamma_\infty = -4.65$ (SEN et al.) we have obtained the value of the quadrupolar coupling constant $e^2qQ/h = 1626$ kHz and the value of the asymmetry parameter $\eta = 0.5$. These theoretical values are in good agreement with experimental values. Our theoretical calculations of the electric field gradients may be

considered, as preliminary ones since the distortion of the oxygen polyhedron and framework for the models B – E (Table 1) are not accounted. It should be also noted that application of simple model of the electric point charges to the calculation of the EFG tensor for ^{27}Al nucleus into AlO$_4$ tetrahedron is not correct (VOROTILOVA et al.). However from the qualitative results represented in Table 1, it follows that contribution of the electric dipolar moments of the water molecules to the electric field gradient on the ^{23}Na sites is comparable with that from the whole lattice. The diffusion of the water molecules induces the averaging of the water contribution to the electric field gradient at ^{23}Na positions and it leads to the decreasing of the ^{23}Na quadrupolar coupling constant. From the temperature dependencies of ^{23}Na NMR spectra it follows so that the diffusion of the sodium ions is absent in natrolite structure. These results indicate that the main contributions to the potential barrier for the sodium ions are given by the electrostatic interactions of sodium ions with the ions of zeolite aluminosilicate framework.

3. Conclusions

From our results on the simulation of ^{1}H NMR spectra for different models of molecular mobility of water molecules in natrolite it may be concluded that in natrolite there is the diffusion of the water along the Schottky defects. The model of the normal distribution of the activation energy may be considered as a preferable model for the diffusion of the water molecules in natrolite. From the temperature dependency of the quadrupolar interaction constant of ^{27}Al nucleus at T < 650 K it follows that the internal mobility of aluminium ions is natrolite is not observed. The increasing of the quadrupolar coupling constant of ^{27}Al nuclei at T > 650 K is connected with the complete dehydration of natrolite. The temperature dependency of the NMR quadrupolar second-order shifts of the two structurally nonequivalent ^{23}Na nuclei indicates that the diffusion of sodium ions is absent in natrolite. The observed small increasing of the quadrupolar coupling constant of ^{23}Na nuclei is connected probably with diffusion of water molecules in the natrolite pores. From our ^{1}H, ^{23}Na, ^{27}Al NMR data it follows that in the temperature range up to 573 K the phase transitions in natrolite, connected with modifications of the aluminosilicate framework or the structure of pores are not observed.

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