

UDK 537.635 541.127

NMR OF ^{23}Na IN NATROLITE

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The temperature dependences of NMR and MAS NMR spectra of ^{23}Na nuclei in Al-natrolite ($\text{Na}_2\text{Al}_2\text{Si}_3\text{O}_{10} \cdot 2\text{H}_2\text{O}$) and Ga-natrolite ($\text{Na}_2\text{Ga}_2\text{Si}_3\text{O}_{10} \cdot 2\text{H}_2\text{O}$) have been studied. It has been shown that the diffusion of the sodium ions at $T < 400$ K is absent in Al- and Ga- natrolites. The temperature dependences of the spin-lattice relaxation times T_1 in Al- and Ga- natrolite have been studied. The influence of the water molecular mobility in the nanochannels of natrolites on the spin-lattice relaxation times of ^{23}Na has been discussed.

Keywords: NMR, magnetic relaxation, zeolite, natrolite, water mobility.

PACS: 76.60.-k; 78.55.Mb

INTRODUCTION

The Al-natrolite ($\text{Na}_2\text{Al}_2\text{Si}_3\text{O}_{10} \cdot 2\text{H}_2\text{O}$) and Ga-natrolite ($\text{Na}_2\text{Ga}_2\text{Si}_3\text{O}_{10} \cdot 2\text{H}_2\text{O}$) are the typical channel-type compound with porous structure [1]. The natrolite framework consist of the chains AlO_4 and SiO_4 tetrahedra linked together via common oxygen atoms. The natrolite structure contains channels running both perpendicular and parallel to the c-axis. The water molecules and ions Na^+ are located in the small nanochannels of natrolite in the form of zig-zag chains [1, 2] Each sodium ion is coordinated by two framework's oxygen atoms and by two water molecules. The sodium cations in the channels of natrolite, as well as water molecules, can possess the certain mobility. However unlike molecules of water they cannot be removed from a crystal if only to not resort by an ionic exchange [2].

The dynamics of water molecule in Al-natrolite have been studied by NMR in [2-4]. From temperature measurements of the spin-relaxation times (T_1 и $T_{1\rho}$) of ^1H nuclei in Al-natrolite it was concluded that in an temperature interval 330 K ÷ 450 K takes place the reorientation of water molecules around of their pseudo-axes of second order symmetry (180° flip motion), and in an interval 450 K ÷ 540 K it has been assumed availability reorientation of water molecules around of the one hydrogen bonds [3]. In the subsequent it has been established, that this second type of water molecules mobility is connected with diffusion of water molecules in the channels of natrolite and the 180° flip motion take place simultaneously with diffusion along the c-axis [2, 4].

The powerful method for the study of zeolites is the NMR of quadrupole nuclei. The NMR of the quadrupole nuclei ^{23}Na in a single crystal of Al-natrolite have been investigated at room temperature in [5, 6]. The obtained quadrupole coupling constant (QCC) and asymmetry parameter of the electric field gradient (EFG) tensor were determined to be: $eqQ/h = 1759$ kHz; $\eta = 0,6427$. From results represented in [4] it

follows that the QCC of ^{23}Na nuclei do not depend on the temperature at $T < 500$ K. However at $T > 500$ K the QCC are decreased and the observed decreasing of the QCC of ^{23}Na nuclei is connected with diffusion of water molecules in the natrolite channels. From the observed temperature independent of NMR spectra of ^{23}Na in Al-natrolite single crystal it was concluded that the translation diffusion of Na ions is absent in the natrolite channels [4].

In the present paper we represent the results of the study of Al- and Ga-natrolites by the ^{23}Na NMR. We investigate the temperature dependences of the ^{23}Na NMR spectra in static and rotated (MAS) samples with and without ^1H decoupling as well as the temperature dependences of the spin-lattice relaxation times of the ^{23}Na nuclei in Al- and Ga-natrolites.

1. EXPERIMENTAL PART

The polycrystalline samples of natural Al-natrolite from Khibiny deposit (Kola Peninsula, Russia) were used in this study. The gallium form of natrolite was hydrothermally synthesized as described in [7]. The ^{23}Na NMR spectra were measured at $\nu_0 = 105.842$ MHz frequency in 9.4 T magnetic field using a Bruker Avance-400 NMR spectrometer. The ^{23}Na MAS NMR spectra were measured using the 4 mm diameter zirconia (ZrO_2) rotor cells equipped with powdered sample rotated under magic angle with 10 kHz frequency. Classical direct acquisitions by single pulse excitations (free induction decay - FID) were used. The ^{23}Na has $I = 3/2$ nuclear spin, and for selective excitation of the central ($m_I = +1/2 \leftrightarrow -1/2$) transition the optimal pulse duration equals to the duration of a non-selective $\pi/2$ pulse divided by $I + 1/2 = 2$ [8]. In our experiments the radiofrequency (RF) pulse $\pi/4 = 1.0 \mu\text{s}$ was used. The NMR spectra were obtained by Fourier transformation of FID signals. The spin-lattice relaxation time T_1 for ^{23}Na nuclei was measured by saturation-recovery method.

The Dmfit program [9] was used to simulate the ^{23}Na spectra to extract the isotropic chemical shifts (δ_{iso}), quadrupolar coupling constants and the asymmetry parameters (η_Q). The Dmfit model of MAS NMR spectrum includes an apodisation of the theoretical lineshape by Lorentzian or Gaussian curves with the broadening parameters $\Delta\nu$, $\Delta\nu_L$ or $\Delta\nu_G$, that indicate a distribution of slightly distinct environment of nuclei.

2. OBTAINED RESULTS AND DISCUSSION

The sodium neighbours in Al- and Ga-natrolites have a configuration of a distorted tetrahedron. In the tetrahedron corners there are two oxygen atoms belonging to a framework and two oxygen atoms of water molecules at an average distances of 2.37 Å. Furthermore there are two oxygen atoms of a framework at an average distances of 2.5 Å, four protons at an average distances of 2.8 Å and atoms of silicon and aluminum at an average distances of 3.0 Å.

The experimental ^{23}Na MAS NMR spectrum of Al-natrolite is shown in Fig. 1, *a*. The rotation of sample at magic angle (MAS NMR) leads to fully average of dipolar interaction of magnetic moments of ^{23}Na with magnetic moments of other nuclei in natrolite ^1H , Si , Al . In this case the shape of NMR spectra is determined only by the second-order quadrupolar shift of the central transition [8]. Using program DMFit [9] we calculated the shape of MAS NMR spectrum of ^{23}Na in polycrystalline natrolite. The result of theoretical calculations are shown in Fig. 1, *b*. The obtained theoretical values of the quadrupolar frequency ν_Q and the asymmetry parameter η well coincide with experimental values obtained in [5].

In Fig. 2 is presented the ^{23}Na MAS NMR spectra obtained in Al-natrolite at $T = 300\text{ K}$ and $T = 380\text{ K}$. These spectra were obtained using the method of ^1H decoupling. NMR ^1H decoupling is a special method used in NMR which allow to eliminate fully the effect of magnetic dipolar coupling between resonance nuclei (^{23}Na in our case) and ^1H nuclei. From the comparison of the ^{23}Na NMR spectra, shown in Fig. 2, it appears that the ^{23}Na NMR spectra have the same shape at $T = 300\text{ K}$ and $T = 380\text{ K}$. The NMR shape of ^{23}Na is determined by magnetic dipolar interactions with other magnetic nuclei and by electric quadrupolar interaction with the electric field gradient (EFG) on the ^{23}Na sites. The interaction with magnetic moment of ^1H nuclei give the main contribution to the magnetic dipolar interaction of ^{23}Na nuclei. However the ^1H decoupling, which was used at recording the NMR spectra of ^{23}Na NMR (Fig. 2), leads to averaging of the dipolar interactions between the magnetic moments of ^1H and ^{23}Na nuclei and so, from Fig. 2, it follows that in the temperature region $T < 380\text{ K}$ the electric field gradient (EFG) at the ^{23}Na sites does not depend on the temperature.

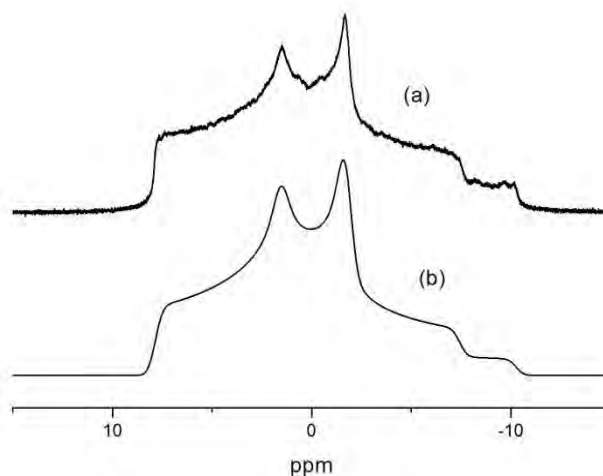


Fig. 1. ^{23}Na MAS NMR spectra of Al-natrolite at $\Omega_{\text{rot}} = 10\text{ kHz}$: (a) experimental spectrum at $T = 300\text{ K}$; (b) theoretical spectrum with parameters $C_Q = 1759,2\text{ kHz}$, $\eta = 0,64$, $\delta_{\text{CSA}} = 8,19\text{ ppm}$, $\Delta\nu_{\text{Gauss}} = 73,11\text{ Hz}$.

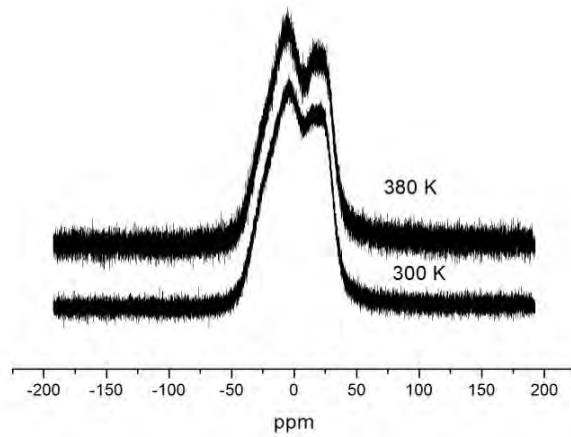


Fig. 2. ^{23}Na NMR spectra with ^1H -decoupling in Al-natrolite at $T = 300\text{ K}$ and $T = 380\text{ K}$.

In natrolite there are two structurally nonequivalent ^{23}Na and 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 [6]. The experimental temperature dependencies of the quadrupolar second-order shift 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. 3 [4]. This result was obtained using the CW NMR spectrometer at a frequency of the of 11 MHz on Al-natrolite single crystals [4].

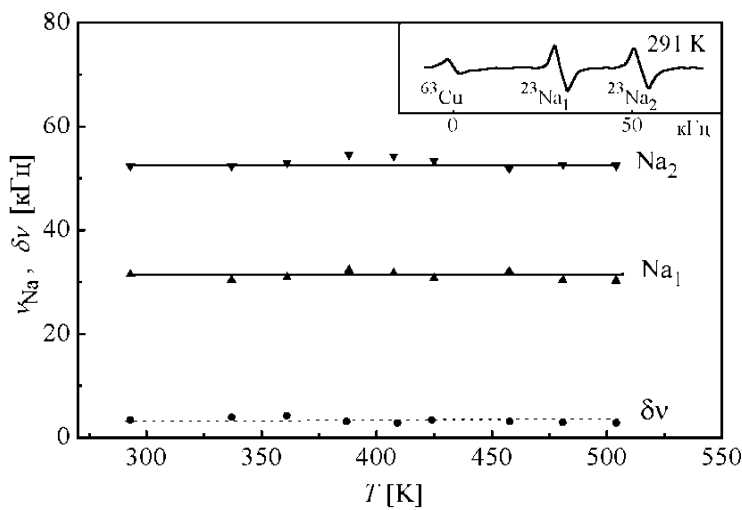


Fig. 3. The temperature dependencies of the second-order quadrupolar shifts and the linewidth ($\delta\nu$) of ^{23}Na NMR spectra for the two structurally nonequivalent ^{23}Na ions in the natrolite single crystal. Inset: the central part of NMR spectrum of ^{23}Na in single crystal.

The intensive diffusion of ^{23}Na cations in natrolite pores should lead to the averaging of the second-order quadrupolar shifts of the two structurally nonequivalent ^{23}Na nuclei. In reality, such effect is not observed (Fig. 3). So, from this result it follows that the diffusion of the sodium ions is absent in natrolite channels in the temperature region $T < 500$ K [4].

The EFG at the ^{23}Na sites in the natrolite structure is determined by the electric charges of the ions of whole lattice and by the electric dipolar moments of the water molecules. According with ^1H NMR data of Al-natrolite the water molecules at $T < 380$ K rotate about their quasi 2-fold axis [3] and the 180° flip motion take place simultaneously with diffusion along the c-axis [2]. These motions of the water molecules must lead to the averaging of the contributions of the electric dipolar moments of the water molecules to EFG at the ^{23}Na sites. If contribution from the electric dipolar moments of water molecules to the EFG tensor at the ^{23}Na sites is considerable the averaging of this contribution must be observable in the temperature dependence of ^{23}Na NMR spectra. From our experimental temperature dependences of ^{23}Na MAS NMR and NMR spectra represented in Fig. 2 and Fig. 3 it follows that this effect is not observed. From this fact we may conclude that the contributions of the electric dipolar moments of the water molecules to EFG at the ^{23}Na sites are very small.

Fig. 4. shows the ^{23}Na NMR spectra obtained without ^1H decoupling at $T = 300$ K and $T = 380$ K. The difference between the NMR spectra represented in Fig. 2 and Fig. 4 are related to the dipolar interactions between the magnetic moments of ^1H and ^{23}Na nuclei. The shape of these NMR spectra is determined not only by the second-order quadrupolar shift of the central transition but also by the dipolar interaction between magnetic moment of ^{23}Na and ^1H nuclei. From Fig. 4 it follows that increasing of the sample temperature leads to thermal averaging of dipolar interactions between the magnetic moments of ^1H and ^{23}Na nuclei. Because from NMR data it follows that the 180° flip motion of water molecules take place simultaneously with diffusion along the c-axis [2] we may conclude that the averaging of dipolar interaction of magnetic moments of the ^{23}Na with magnetic moments of protons is connected with the rotations of water molecules about their quasi 2-fold axis and with diffusion of water molecules across canals in natrolites [4].

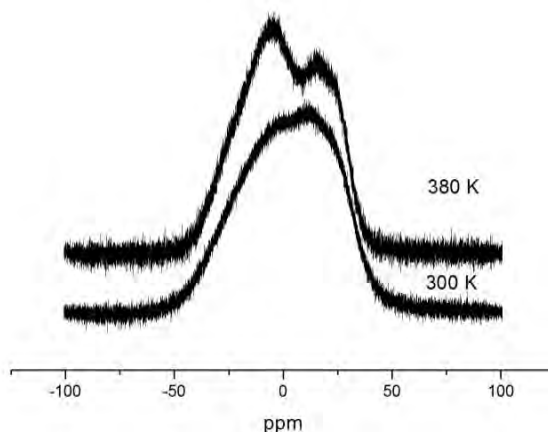


Fig. 4. ^{23}Na NMR spectra without ^1H -decoupling in Al-natrolite at $T = 300$ K and $T = 380$ K.

The temperature dependence of the spin-lattice relaxation times T_1 of ^{23}Na in Gnatrolite is shown in Fig. 5. The similar temperature dependence is observed in Alnatrolite.

In order to identify the main causes of the measured ^{23}Na relaxation times in natrolite, we consider the theoretical calculations of T_1 on the basis of different dynamical model. The physical mechanisms which could be induce the longitudinal relaxation of the ^{23}Na nuclei are [10]:

- (i) spin-phonon interactions – interactions of the quadrupolar electric moment of the ^{23}Na nuclei with the crystal electric field gradient modulated by lattice vibrations;
- (ii) dipolar interaction with paramagnetic impurities (for example with Fe^{3+});
- (iii) magnetic dipolar interaction with absorbed ions or molecules and with magnetic moments of ^{27}Al (^{71}Ga , ^{69}Ga), ^{29}Si , ^1H and other ^{23}Na nuclei of natrolite structure;
- (iv) electric quadrupolar interactions with the crystal electric field gradients modulated by motion of charge cations or water molecules [10]. These motions are the “hopping” motions, i.e. the atoms or water molecules spend most of their time in potential well corresponding to equilibrium positions, and only a very small fraction move between these potential wells.

The phonon-based relaxation mechanism could not be the cause of spin-lattice relaxation of the quadrupolar nuclei in natrolites. From obtained estimations it follows that if relaxation were to proceed by this mechanism the values of T_1 for quadrupolar nuclei in zeolites at room temperature should be 4-5 orders of magnitude larger than the experimental values [10]. The spin-lattice via paramagnetic impurities may be significant only at very low temperature [10]. The magnetic dipolar interaction could not be also the cause of the spin-lattice relaxation of the ^{23}Na nuclei in natrolite. From our estimations we obtain that the dipolar interactions of the ^{23}Na with magnetic moments of the proton magnetic moment give the minimal value of the spin-relaxation time $T_{1\text{min}}$ equals ~ 5 s, which much larger than experimental values 0,04 s (Fig. 5). So only one mechanism (iv) need to be considered.

It is known that the relaxation of the quadrupolar nuclei may be multiexponential [11, 12]. However, for selective saturation of the central transition [8], the relaxation is well described by single exponential [13]. In our case the translational and reorientational jumps of water molecules modulate only the part of EFG tensor concerned with electric dipolar moments of water molecules. The remaining part of the EFG tensor given by the electric charges of the ions of whole lattice is not changed. So the quadrupolar relaxation concerned with modulation of the part of EFG at the site of the quadrupolar nuclei as a result of the activated translational and reorientational jumps of electric dipoles of water molecules may be described ($I = 3/2$) by equation [10, 12, 13]

$$T_{1Q}^{-1} = 9 \left(1 + \frac{\eta^2}{3} \right) \Delta C_Q^2 \frac{\tau_c}{1 + \omega_0^2 \tau_c^2}, \quad (2)$$

where ω_0 is the Larmor frequency of the quadrupole nucleus; η – asymmetry parameter of EFG tensor and

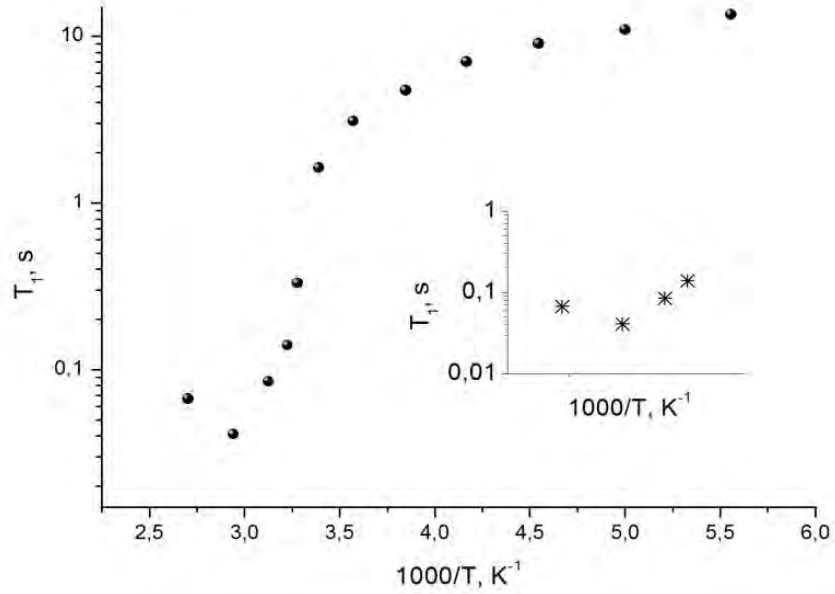


Fig. 5. The temperature dependences of the spin-lattice relaxation time of the ^{23}Na nuclei in Ga – natrolite.

$$\Delta C_Q = \frac{e^2 \Delta q Q}{\hbar} . \quad (3)$$

Here $e\Delta q$ describes the part of EFG at the site of the ^{23}Na nuclei connected with the electric dipoles of water molecules.

From Eq. (2) it follows that minimal value of T_{1Q} for selective saturation and detection of the central transition is observed at $\omega_0 \tau_c = 1$ and is equal

$$T_{1\min} = \frac{4\pi\nu_0}{3(3 + \eta^2)\Delta C_Q^2} . \quad (4)$$

For the ^{23}Na nuclei in the natrolite $T_{1\min} \cong 0.04$ s. Using $\eta = 0,64$ and $\nu_0 = 105,542$ MHz we obtain from Eq. (4)

$$\Delta C_Q \approx 56,93 \text{ kHz} . \quad (5)$$

The full constant of quadrupolar interaction $C_Q = 1759,3$ kHz and so from our result it follows that the contributions of the electric dipolar moments of the water molecules to full EFG at the ^{23}Na sites are 3.2% only.

CONCLUSION

From analysis of the temperature dependencies of NMR and MAS NMR spectra of ^{23}Na nuclei (with and without ^1H -decoupling) it follows that the diffusion of the sodium ions at $T < 400$ K absents in Al- and Ga- natrolites. From analysis of NMR spectra of ^{23}Na nuclei (with and without ^1H -decoupling) it follows that in Al- and Ga-natrolites the 180° flip motion of water molecules take place simultaneously with diffusion of the water along the Schottky defects. The obtained from ^{23}Na MAS NMR spectrum theoretical values of the quadrupolar frequency ν_Q and the asymmetry parameter η well coincide with experimental values obtained early. The spin-lattice relaxation of the ^{23}Na is governed by the electric quadrupole interaction with the crystal electric field gradients modulated by translational motion of H_2O molecules in the natrolite pores. The dipolar interactions with paramagnetic impurities become significant as a relaxation mechanism of the ^{23}Na nuclei only at low temperature (< 270 K).

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В Al-натроліті ($\text{Na}_2\text{Al}_2\text{Si}_3\text{O}_{10} \cdot 2\text{H}_2\text{O}$) та Ga-натроліте ($\text{Na}_2\text{Ga}_2\text{Si}_3\text{O}_{10} \cdot 2\text{H}_2\text{O}$) вивчені температурні залежності спектрів ЯМР і MAS ЯМР ядер ^{23}Na . Було показано, що в Al-натроліті та Ga-натроліті при $T < 400$ К відсутня дифузія іонів натрію. Отримано температурні залежності часу спин-граткових релаксації T_1 в Al-натроліті і Ga-натроліті. Обговорюється вплив молекулярної рухливості води в наноканалах структури натроліта на спин-граткову релаксацію іонів ^{23}Na .

Ключові слова: ЯМР, магнітна релаксація, цеоліти, рухливість води, натроліт.

Пачва М. ЯМР ^{23}Na в натролите / М. Пачва, А. А. Сапига, М. Ольшевски, Н. А. Сергеев, А. В. Сапига // Ученые записки Таврического национального университета имени В. И. Вернадского. Серия : Физико-математические науки. – 2014. – Т. 27 (66), № 2. – С. 70-78.

В Al-натролите ($\text{Na}_2\text{Al}_2\text{Si}_3\text{O}_{10} \cdot 2\text{H}_2\text{O}$) и Ga-натролите ($\text{Na}_2\text{Ga}_2\text{Si}_3\text{O}_{10} \cdot 2\text{H}_2\text{O}$) изучены температурные зависимости спектров ЯМР и MAS ЯМР ядер ^{23}Na . Было показано, что в Al-натролите и Ga-натролите при $T < 400$ К отсутствует диффузия ионов натрия. Получены температурные зависимости времени спин-решеточной релаксации времени T_1 в Al-натролите и Ga-натролите. Обсуждается влияние молекулярной подвижности воды в наноканалах структуры натролита на спин-решеточную релаксацию ионов ^{23}Na .

Ключевые слова: ЯМР, магнитная релаксация, цеолиты, подвижность воды, натролит.

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Received 21 September 2014.