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NMR STUDY OF THE DIFFUSION OF WATER MOLECULES IN NATROLITE

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The mineral natrolite ($Na_2Al_2Si_3O_{10}2H_2O$) is the typical channel-type compound with porous structure (zeolite). The natrolite unit cell is orthorhombic with space group *Fdd*2 [1, 2]. The water molecules are situated at regular positions within the channels and form hydrogen bonds to oxygens of the aluminosilicate structure. According to the NMR and neutron diffraction data all water molecules are chemically and structurally equivalent at the room temperature [2-4]. The dynamic of water molecules in the natrolite has been studied by NMR [5-7]. 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° 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 [7]. The chemically and structurally equivalence of water molecules suggests that the diffusive jumps of water molecules may be characterized by the same correlation time τ_c. However, this suggestion does not agree to observed temperature transformations of the NMR spectra [8, 9].

In this study we have undertaken a detailed investigation of the temperature dependencies of the NMR spectra of a natrolite single crystal. A clear natrolite single crystal $5 \times 6 \times 10$ mm^3 in size was used. The orientation of the crystal was carried out on the basis of X-ray data. Absorption NMR spectra were obtained with a 30 MHz NMR spectrometer at various crystal orientations in external magnetic field ($\mathbf{B}_0$).

The experimental temperature dependence of the NMR spectrum for the case when $\mathbf{B}_0$ is parallel to *a* crystallographic axis is given in Fig.1A. In this case all H-H vectors of the H_2O molecules are magnetically equivalent and NMR spectrum of rigid water molecule is the Pake doublet with splitting $\Delta\nu = 4.5$ kHz [4]. At the room temperature the lines of this doublet are not resolved, as a result of the intermolecular dipolar H-H interactions. The diffusion of water molecules leads to the motional average of the intermolecular dipolar H-H interaction and the well-resolved Pake doublet is observed at the high temperature (Fig. 1A.4). The value of high temperature doublet splitting is same as $\Delta\nu$ for the rigid water molecule [7]. This fact suggests that the water molecules diffuse along the regular positions of water molecules in the natrolite structure. The experimental temperature dependence of the NMR spectrum for the case when the vector $\mathbf{B}_0$ lies in (*ac*)-plane of the crystal at an angle 45° with *c*-axis is given in Fig. 2A. For this case the theoretical NMR spectrum contains two Pake doublets with splitting $\Delta\nu_1 = -45.5$ kHz and $\Delta\nu_2 = 41.3$ kHz [4]. At the 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 the non-resolved doublets. The heating of the crystal induces the motional average of the intra- and intermolecular dipolar H-H interactions and at the high temperature the single narrow doublet is observed (Fig. 2A. 6). The value of the splitting of this doublet coincides with the average value $(\Delta\nu_2 + \Delta\nu_1)/2$ [7]. This fact independently supports the suggestion that the water molecules diffuse along the Schottky defects [10].

In order to explain the observed temperature transformations of the NMR spectra we have assumed that the diffusion jumps of water molecules may be characterized by the same correlation time τ_c.

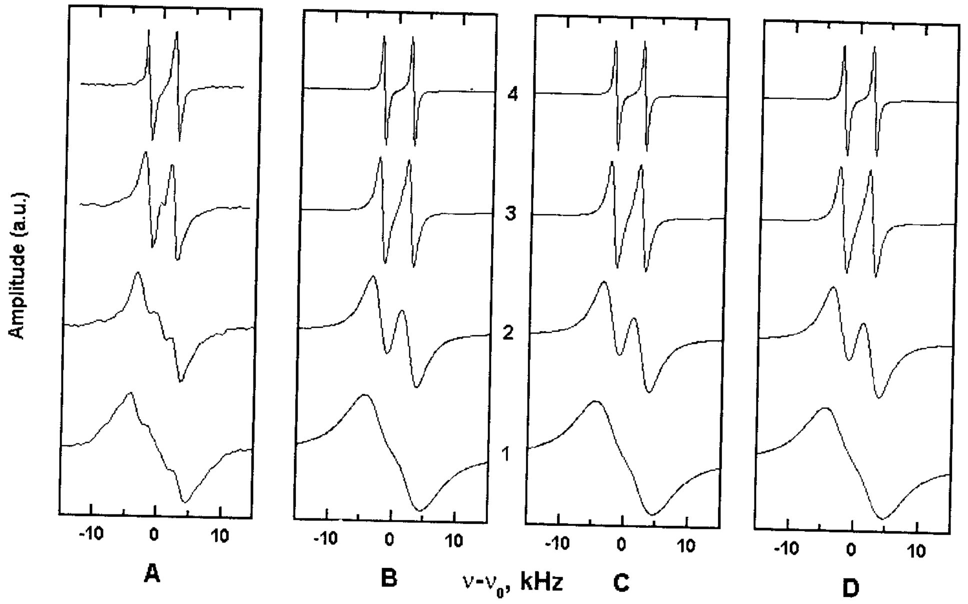

Fig. 1. The temperature dependencies of the NMR spectra of natrolite for the case when vector $\mathbf{B}_0$ is parallel to *a* crystallographic axis. A – the experimental NMR spectra. B – the theoretical spectra obtained for the model of homogeneous diffusion of water molecules with the activation energy $E_a = 62.8$ kJ/mol. C – the theoretical spectra obtained for the model of heterogeneous diffusion of water molecules with the activation energies $E_{a1} = 46$ kJ/mol and $E_{a2} = 72.3$ kJ/mol; the ratio of water molecules in different dynamical phase is 1 : 1. D – the theoretical spectra obtained for the model of the normal distribution in the activation energy ($E_a = 62.8$ kJ/mol and $\sigma_E = 10.5$ kJ/mol). 1 – $T = 294$ K; 2 – $T = 333$ K; 3 – $T = 393$ K; 4 – $T = 443$ K

Using the stochastic Liouville equation for the spin density matrix [11, 12] we obtain the following expression for the NMR spectrum of the water molecule jumping along the two sites:

$$g(\Delta) = A[f(\Delta) + f(-\Delta)]\,, \tag{1}$$

where

$$f(\Delta) = \frac{\dfrac{(\nu_1 - \nu_2)^2}{\tau_c} + \dfrac{(\nu_1 - \nu_2)^2 + 2(\nu_1 + \Delta)(\nu_2 + \Delta)}{T_2} + \dfrac{2}{T_2}\left(\dfrac{2}{\tau_c} + \dfrac{1}{T_2}\right)^2}{\left[(\nu_1 + \Delta)(\nu_2 + \Delta) - \dfrac{1}{T_2}\left(\dfrac{2}{\tau_c} + \dfrac{1}{T_2}\right)\right]^2 + \left(\dfrac{1}{\tau_c} + \dfrac{1}{T_2}\right)^2 (\nu_1 + \nu_2 + 2\Delta)^2} \tag{2}$$

Here $\Delta\nu = \nu - \nu_0$; $\nu_0 = \gamma \mathbf{B}_0/2\pi$ is the Larmor frequency of the ^{1}H nuclei; τ_c is the correlation time which defines the average time between jumps of water molecule from one equilibrium site to another one; the parameter T_2 is the spin-spin relaxation time and this parameter is defined by the intermolecular dipolar interaction between protons of different water molecules.

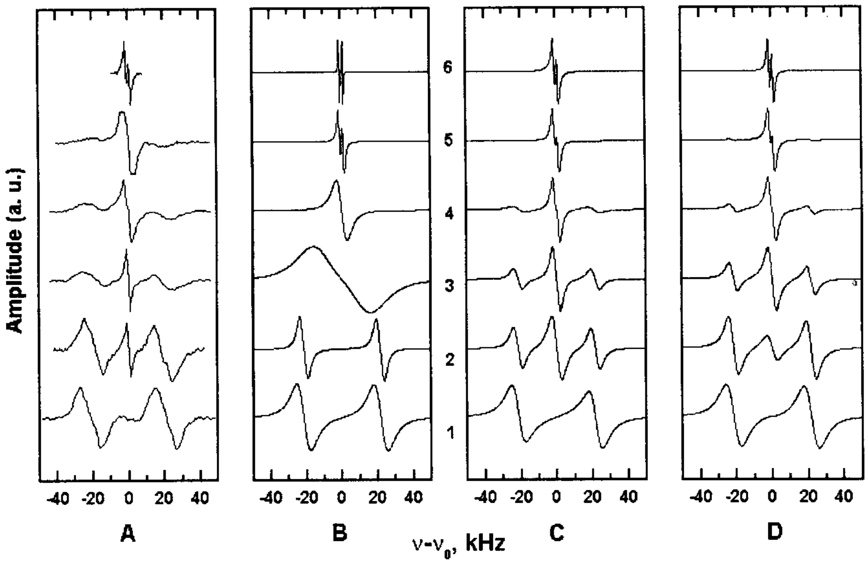

Fig. 2. The temperature dependence of the NMR spectrum of natrolite for the case when vector $\mathbf{B}_0$ lies in (*ac*)-plane at an angle 45° with *c*-axis. A – the experimental spectra. B – the theoretical spectra obtained for the model of homogeneous diffusion of water molecules with the activation energy E_a = 62.8 kJ/mol. C – the theoretical spectra obtained for the model of heterogeneous diffusion of water molecules with the activation energies E_{a1} = 46 kJ/mol and E_{a2} = 72.3 kJ/mol; the ratio of water molecules in different dynamical phase is 1 : 1. D – the theoretical spectra obtained for the normal distribution in the activation energy ($\bar{E}_a$ = 62.8 kJ/mol and σ_E = 10.5 kJ/mol). 1 – T = 293 K; 2 – T = 375 K; 3 – T = 423 K; 4 – T = 453 K; 5 – T = 493 K; 6 – T = 543 K

In Eq. (2)

$$\nu_i \equiv \frac{\Delta\nu_i}{2} = \frac{3}{4}\mu R^{-3}(1 - 3\cos^2\theta_i) , \tag{3}$$

where μ is the proton magnetic moment, θ_i is the angle between the H-H vector in the *i*-site and vector $\mathbf{B}_0$; R is the distance between the protons of the water molecule.

The theoretical temperature dependencies of the NMR spectra are shown in Fig. 1B and Fig. 2B. These spectra have been obtained using Eqs. (1)-(3) and assuming that τ_c fulfills an Arrhenius activation law

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

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 agreement with experiment.

The existence of the additional spectral lines in the central part of NMR spectra (Fig. 2A.2-6) may be explained only assuming that there is dynamic heterogeneity of the water molecules.

Fig. 1C and 2C show the theoretical temperature dependencies of NMR spectra obtained in assumption that there are two kind of water molecules with the activation energies E_{a1} and E_{a2} The agreement between the experimental data and the fitted NMR spectra is good over the whole temperature range. However, we assume that the model of two activation energies for the diffusion of the water molecules in natrolite is not reasonable and one is hardly explainable.

There is plenty of evidence in the literature [13, 14] to suggest that the molecular diffusion in solids is not characterized by the single correlation time. We have assumed that a distribution in 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

$$f(E_a) = B\exp\left[-\frac{1}{2}\frac{(E_a - \overline{E_a})^2}{\sigma_E^2}\right]$$

It is well known that a normal distribution in E_a leads to the log-normal distribution of the correlation time τ_c [13].

The theoretical NMR spectra obtained for the case of the normal distribution in the activation energy E_a are shown in Fig. 1D and Fig. 2D. From the good agreement between the experimental and simulated NMR spectra it can be conclude that the model of the normal distribution in the activation energy may be considered as a preferable model for the diffusion of the water molecules in the natrolite.

We hope the computer simulations of the diffusion processes by the molecular dynamic methods will allow understand of the nature of the activation energy distribution in the natrolite.

References

[1] W. M. Meier, Z. Kristallogr. **113**, 430 (1960).

[2] B. H. Torrie, I. D. Brown, H. E. Petch, Can. J. Phys. **42**, 229 (1964).

[3] S. P. Gabuda, A. G. Lundin, G. M. Mikhailov, K. S. Aleksandrov, Sov. Phys.-Crystallogr. **8**, 305 (1963).

[4] A. V. Sapiga, N. A. Sergeev, V. N. Szcherbakov, S. P. Gabuda, I. A. Belisky, J. Struct. Chem. **27**, 181 (1986).

[5] S. P. Gabuda, Dokl. Akad. Nauk USSR, **146**, 840 (1962).

[6] R. T. Thompson, R. R. Knispel, H. E. Petch, Can. J. Phys. **52**, 2164 (1974).

[7] A. V. Sapiga, N. A. Sergeev, V. N. Szcherbakov, S. P. Gabuda, I. A. Belisky, J. Struct. Chem. **27**, 183 (1986).

[8] A. V. Sapiga, N. A. Sergeev, S. P. Gabuda, in: *Chemistry and Physics of Solid State*, ONI ITEChim, N 1161, 54 (1983) (in Russian).

[9] A. V. Sapiga, S. N. Polulyakh, in: Proceedings of the Joint 29th AMPERE – 13th ISMAR International Conference *Magnetic Resonance and Related Phenomena* (Ed. D. Ziessow, W. Lubitz, F. Lendzian) Berlin, II, 650 (1998).

[10] N. A. Sergeev, O. V. Falaleev, S. P. Gabuda, *Sov. Phys. Solid State* **11**, 2248 (1969).

[11] J. I. Kaplan and G. Fraenkel, *NMR of Chemically Exchanging Systems*, Academic, N. Y. (1980)

[12] N. A. Sergeev, E. M. Kipperman, A. M. Vakhrameev, M. L. Afanasjev, J. Struct. Chem. **22**, 83 (1981).

[13] H. A. Resing, J. Chem. Phys. **43**, 669 (1965).

[14] A. F. Privalov and I. V. Murin, Phys. Solid State **41**, 1482 (1999), and references given therein.