ANOMALOUS TEMPERATURE DEPENDENCE OF SOLID-ECHO SIGNAL IN NANOPOROUS NATROLITE

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The mineral natrolite (Na2Al2Si3O10·2H2O) is the compound with nanoporous structure. The small nanochannels in the structure of natrolite have dimensions of the order 0.3 nm and the water molecules and ions Na⁺ are located in them in the form of zig-zag chains [1]. From experimental data on dehydration of natrolite it follows that after heating the sample up to the temperature of ~ 200°C the natrolite loses not more than 5% of the zeolite water [2]. NMR data indicate that water molecules diffuse along the channels among the vacancies whose positions coincide with the regular position of water molecules in crystal lattice [3]. In present communication we represent the experimental results on the study of the temperature dependence of solid-echo signal (pulse sequence 90° − τ − 90° − τ). In our experiments we observed unusual (“anomalous”) temperature dependence of solid-echo signals: in the temperature range of 40° – 130° at some temperatures the maximum of the echo signal is shifted toward the end of the second RF pulse and the echo signal is lost in the region of the dead time after the second pulse (fig.1). These “anomalous” temperatures are shown in fig.2 by the dark circles. It should be noted that the value of the temperature at which the echo signal vanishes depends on a thermal history of a sample and on how long the crystal was kept at given temperature.

The influence of molecular motions on the solid-echo signal was investigated in [4-6]. It was shown that the internal molecular motion in solids can reduce the echo amplitude and can shift it toward the end of the second RF pulse. This effect is observed when the correlation time τc describing the mobility fulfils the following conditions: τc ≈ τ and τc√M2 ≈ 1, where τ is the delay between RF pulses and M2 is the second moment of NMR spectrum. From these results we may assume, that observed vanishing of solid-echo

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Fig.1. The shape of solid-echo signal at different temperature

Fig.2. The temperature dependence of the amplitude of solid-echo signal
signal at some temperature is connected with anomalous behaviour of the correlation time $\tau_c$. The anomalous temperature behaviour of $\tau_c$ precisely in the natrolite was observed in [7,8]. It was observed that the value of the correlation time $\tau_c$ at given temperature is strongly depends on a thermal history of a sample and on how long the crystal was kept at fixed temperature. The dependence of the correlation frequency $\nu_c = 1/\tau_c$ of diffusion of water molecules in natrolite vs. the time of the localization of sample at given temperature is shown in fig.3.

It should be noted that the anomalous temperature behaviour of $\tau_c$ is reflected also in the temperature dependences of NMR spectra, which were explained by non-Markovian character of the diffusion of water molecules in natrolite [9].

Apparently, the anomalous temperature behaviour of $\tau_c$ is connected with the fact, that the channels in the crystal structure of natrolite are very narrow and the diffusion of water molecules is connected with the large deformations of the aluminosilicate framework. These deformations lead to dynamical heterogeneity of the ensemble from the water molecules or to the strong spread of the correlation times [10].

![Fig.3. The time dependence of the correlation frequency $\nu_c = 1/\tau_c$ at $T = 210^\circ$C [7]](image)