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NMR method used for investigation of water mobility in porous crystal

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1. Introduction

Usually the NMR investigations of molecular mobility in a solid state are based on study of temperature dependence of second moment (M_2) and determination of activation energy. The other method is basing on the analysis of local magnetic field tensor [1]. However from the analysis of NMR line-shape in monocrystals at temperature range of slow and middle motion is possible to obtain the additional information about type of molecular mobility, paths of diffusion and distribution of correlation time and distribution of energy barriers [2,3]. For this purpose it is necessary to study the NMR line shape in the temperature range, in which a width of NMR spectrum will be comparable to molecular motion frequency ($\nu_c \sim M_2^{1/2}$). But some features of NMR line-shape modifications in solid state have remained not study till now, that restricts of the NMR method application for research of molecular motion.

The natrolite ($Na_{16}[Al_{16}Si_{24}O_{80}]\cdot 16H_2O$) is a good model object for examination of a water molecules regular diffusion. The natrolite structure contains channels running both perpendicular and parallel to the **c** axis of crystal. The sodium ions and water molecules are located into these porous. In the natrolite for temperatures higher than 270 K a water molecules diffuse at regular positions [3].

2. Method and results

We investigated the influence of water diffusion in natrolite channels on Pake doublets by the method of a line-shape analysis in temperature range of slow and middle motion [2,3]. The method of a line-shape analysis consists in calculation the theoretical shape of a spectrum on the base of structural dates and hypothetical mechanism of molecular mobility and subsequent comparison the shapes of a spectrum with experimental results. Earlier were known main features of influence a regular diffusion on a shape of NMR spectra [4]. For example in the temperature range of slow motions ($\nu_c < M_2^{1/2}$) the doublet splitting are decreasing (Fig. 1). At the middle range ($\nu_c \sim M_2^{1/2}$) the superposition a broad doublet and narrow line and at the range of fast motion ($\nu_c > M_2^{1/2}$) the narrow doublet are observed [5]. Besides in the range of slow motions doublet components are broadening (Fig. 1). Only narrow doublet in the temperature range of fast motion had a good explanation [1,4]. It is shown [6] that the form of spectrum is determined by effects of frequency exchange in the temperature range averaging of Pake doublet's. For example, the decreases of doublet splitting and the broadening of doublet components in the temperature range of slow motions are largely determined by frequency exchange (Fig. 1). Earlier this change of doublet splitting was explained by influence of vibration motion of the water molecule [4]. However a vibration motion of water molecules can only partially explain of a spectra changes in the range of slow motions.

The composite spectra observed in the temperature range of middle motions [5] was explained as a result of frequency exchange when take place distribution of correlation time. The distribution of correlation times for molecular diffusion is result of nonuniform distribution of water vacancies in neighbor water position and complicated potential landscape, or presence nonequivalent paths for diffusion with different barriers. These and other physical reasons make a diffusion process in channel structures occur as non-Markovian stochastic process [5]. Using this method from temperature dependence of the spectrum shape it is a possible determination of activation energy and a wide of distribution of barriers height for the diffusion process, a types and frequency of molecular motion. It is also a possible determination of trajectories for diffusion in crystal structure. Unfortunately all these opportunities of this method can be realized only in some cases, for example in natrolite.

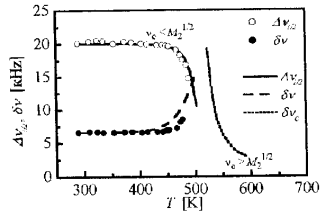

Figure 1: The temperature dependence half of doublet splitting ($\Delta\nu_{1/2}$), the width of doublet components ($\delta\nu$) and the width of central component ($\delta\nu_c$) in natrolite ($\mathbf{B}_0$||[110]). Points are experimental and lines are calculated values. The calculated values at the Figure obtain for water molecule jumping between two positions in crystal and for assumption of the single correlation time [5].

References

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[5] Look at the Fig. 1 in our other report: Olszewski M., Sergeev N. A., Sapiga A. V. - Molecular mobility in natrolite and NMR line shape. (*NMRCM 2004*).

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