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The study of polymorphic states of paradichlorobenzene by means of nuclear quadrupole resonance relaxometry

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ABSTRACT

The article describes the results of the experimental study of the molecular crystal of paradichlorobenzene in α- and β-phases by means of NQR-relaxometry with the inversion of Laplace transformation. The anisotropy effect of the pore space of wood on the distribution of times of the spin-lattice relaxation of p-$C_6H_4Cl_2$ in the pores of pre-impregnated with the molten sample is shown. It was established that the increase in the T_1 spin-lattice relaxation time of ^{35}Cl nucleus in the wood pores (channels) is observed in the case when the radio frequency field B_1 is parallel to the tracheid's of wood. The NQR $T_{1\rho}$ dispersion analysis of paradichlorobenzene in α-phase was carried out for the first time.

1. Introduction

Polymorphic transformations are phase transitions, causing rearrangements of molecules in crystals. However, it is quite a challenge to propose mechanisms that could explain what is actually happening to the molecules in time and space. The Nuclear Quadrupole Resonance (NQR) can be instrumental in studying phase transitions in molecular crystals. The relaxation of the NQR signals in solids depends significantly on the degree of ordering in the sample.

Our previous article [1] describes the results of the experimental study of phase transitions in molecular crystal of paradichlorobenzene by means of the NQR-relaxometry with the inversion of Laplace transformation. We measured the distribution of relaxation times T_1, $T_{1\rho}$ and T_2^* for α- and β-phases of p-$C_6H_4Cl_2$. The distributions of the spin-spin relaxation times T_2 for both phases (α and β) are unimodal and the most probable values of T_2 for α-phase are approximately 4 times less than for the β-phase. Unlike the distribution of T_2 times, the distribution of spin-lattice relaxation T_1 times in the α and β phases of paradichlorobenzene are multimodal. The multimode character of distribution of spin-lattice relaxation time T_1 is presumably caused by the formation of a mixture of amorphous and crystalline materials.

The solution of the diffusion-relaxation equation for the nuclear magnetization with the exponential change of the relaxed state in the surface layer of microcrystals was produced for the interpretation of the relaxation times distribution in [2]. It was shown that the modality of the distribution of relaxation times is determined by the diffusion coefficient of nuclear magnetization and by the distribution of local inhomogeneities near the surface. The results of the experimental study of the influence of the environment, which surrounded the crystallites surface of the powder, on the distributions of spin-spin and spin-lattice relaxation times for the ^{35}Cl nuclei are presented in paper [3]. T_1–T_2 and $T_{1\rho}$–T_2-correlations were worked out by means of 2D-Laplace inversion, and the efficiency of the method for studying the surface phenomena in solids was shown. The study of size effects by NQR enabled us to propose a new method [4] to measure the size of microcrystals containing quadrupole nuclei.

In this work we propose to apply ^{35}Cl NQR relaxometry method to study phase transitions. According to Reynolds [5], the first-order phase transitions are martensitic transformations in all molecular crystals. However, in [6] the experiments reveal the difference between the α→β and β→α transitions in paradichlorobenzene that was seen before. After several cycles of α→β→α phase transitions in the single-crystal sample [7] with each cycle there was a decrease in the intensity of the NQR signal associated with the α-phase. There was a slight increase in the phase transition temperature after each cycle of transitions. This suggests that there is a slight decrease in the degree of order in molecular orientations.

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The processes of phase transitions in the mono- and polycrystalline paradichlorobenzene run in different ways. For the single-crystal sample, the $\beta \to \alpha$ transition goes on more slowly than $\alpha \to \beta$ transition. The $\alpha \to \beta$ phase transformation runs more rapidly in polycrystalline samples than in single crystals [7].

In work [8] the effect of grinding of p-$C_6H_4Cl_2$ powder in α- and β-phases on the width and intensity of the ^{35}Cl NQR lines was studied. It was found that the line width in the β-modification did not change, while for α-modifications the grinding of the powder resulted in the line width broadening and a decrease in the line intensity followed by the restoration of these parameters over time. This enabled the authors to assume that this effect is likely to have been causes by the dislocations, whose stress fields vary in inverse proportion to the distance, i.e. slightly changing and extended stress fields.

As the literature overview shows, the characteristics of polymorphic states, the mechanisms of polymorphic transitions in paradichlorobenzene (p-$C_6H_4Cl_2$) have not been studied in due detail. The aim of this work was to study the phase states in the paradichlorobenzene by means of ^{35}Cl NQR relaxometry technique involving the inversion of Laplace transformation and the $T_{1\rho}$ dispersion analysis method.

2. Experimental study

The ^{35}Cl NQR experiments were performed on the Tecmag Apollo NMR spectrometer with TNMR software. In order to measure the spin-lattice relaxation time $T_{1,}$ the pulse sequence of inversion-recovery 180°–τ–90° was used. The spin-echo pulse sequence of Carr–Purcell–Meiboom–Gill (CPMG) was applied for the measurement of the spin–spin relaxation time T_2.

The NQR is distinctive by in the fact that the equilibrium magnetization is zero. A single pulse with the duration $\tau_{90°}$ set to maximize the NQR signal is referred to as 90°. It should be noted that a simple classical picture, which corresponds to the rotation of nuclear magnetization by 90, is not applicable. The duration of the 180° pulse is about twice as long as the duration of the 90° pulse.

The $T_{1\rho}$ relaxation time is the time constant of the magnetization decay in the rotating frame along the radio frequency (r.f.) field B_1, under the impact of the spin-locking pulse. To measure the relaxation time of $T_{1\rho}$, the first 90° pulse excites nuclear magnetization and then the spin-locking pulse is applied to it. The phase of this pulse is shifted by 90° with regard to the phase of the first excitation pulse so that the direction of the B_1 field of the spin-locking pulse coincides with the vector of the spin magnetization in the rotating frame. During the spin-locking pulse, initially a large magnetization vector decreases and tends to its equilibrium value in the B_1 field, with the time constant $T_{1\rho}$. The spin-lattice relaxation time $T_{1\rho}$ in the rotating coordinate system is measured by analyzing the drop in the NQR signal intensity, depending on the duration of the spin-locking pulse. The experimental data are represented as the following dependence

$$S(\tau) = \int f(T_{1\rho}) \exp\left(-\frac{\tau}{T_{1\rho}}\right) dT_{1\rho} + err \tag{1}$$

Here $f(T_{1\rho})$ is the desired distribution function, τ is the duration of the spin-locking pulse, *err* is the unknown error term. Then, the data were analyzed with the use of the inversion of Laplace transformation. The spin-locking pulse duration in the experiments is varied logarithmically from 0.012 ms to 100 ms. The frequency $\omega_1 = \gamma B_1$ also changed logarithmically from 0.1 kHz to 75 kHz. These pulse sequences are well known from literature and do not require a special description. To study the time processes we used the script “Kinetics Exp” from TNMR software package.

To produce the inversion of Laplace transformation, the program RILT (Regularized Inverse Laplace Transform) was used, described by Marino in [9]. The required array of relaxation time distribution is the inverse Laplace transformation from the set of exponentially decaying signals in the time domain, which is measured as the array of $S(t)$. The $f(T)$ distribution is calculated with the use of regularization by the method of least squares. From 50 to 200 iterations were used while carrying out calculations. The inversion of Laplace transformation was effectively used by us earlier [10,11] in studying microcomposite and porous materials.

Chemically pure commercial polycrystalline samples of the p-dichlorobenzene and potassium chlorate were used in the experiments. Dry wood (pine) was chosen as porous material with anisotropic porous space. A wooden stick in a weighing bottle with melted paradichlorobenzene was left for 24 h in an oven with a view to getting wood impregnated with liquid sample. Then, the stick was removed from the melt, and afterwards it was cooled to room temperature. The wood surface was cleaned of the sample residue.

The structure of the pine wood consists of tracheid (dead elongated spindle-shaped cells) by 90%. As a result the tracheid's pore space is created. The pore sizes are as follows: length is 2–5 mm, the average radius is about 10–50 µm. There are two types of tracheids: early and late ones, with the latter being about 2–3 times smaller in cross dimension.

The choice of paradichlorobenzene (p-$C_6H_4Cl_2$) as a sample is determined by the fact that it has low phase transition temperatures, and also by the fact that this sample was studied by a wide range of experimental techniques, including the NQR spectroscopy [7,8,12,13]. Samples were produced from molten mass in ampoules of 3 cm in length and 1 cm in diameter, and they were composed of numerous small crystals with random orientations. The crystalline phase of the sample was identified using the known temperature dependences of ^{35}Cl NQR frequencies for different phases of paradichlorobenzene. The crystallographic structures of the phases of p-$C_6H_4Cl_2$ are known and described, for example, in [14].

3. Results and discussion

The results of the investigation of the ^{35}Cl NQR spectrum changes of paradichlorobenzene in the transition from α-phase to the γ-phase and back in free slow heating in the air from the temperature of $T = 77$ K to room temperature, are illustrated in Fig. 1. The dependence of the NQR frequency on temperature results in the displacement of spectral lines when the sample is heated. The temperature of the sample was determined by means of the NQR frequency from the known dependence on temperature. The sample in an ampoule was cooled to the temperature of $T = 77$ K outside the working coil, then it was quickly transferred to the coil for measurements.

The transition of paradichlorobenzene from α-phase to the γ-phase and the back manifests itself in the ^{35}Cl NQR frequency hopping. In the case of phase transition $\gamma \to \alpha$ at the temperature of $T = 244$ K two ^{35}Cl NQR lines are observed simultaneously at the frequency range of 430 kHz (Fig. 2).

The structural phase transition in the paradichlorobenzene from β-phase to the α-phase and to the γ-phase with the temperature change and the frequency ^{35}Cl NQR registration was studied earlier in [12,13,15]. In these studies several methods for the preparation of the sample in each phase were proposed including the use of time delay at a certain temperature and the application of mechanical impact or cooling by evaporating acetone or other volatile substances.

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