
LATTICE DYNAMICS
AND PHASE TRANSITIONS

^2H NMR Investigation of the Transition to the Proton Glass State in the $\text{Cs}_5\text{H}_3(\text{SO}_4)_4 \cdot 0.5\text{H}_2\text{O}$ Crystal

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Abstract—A crystal of the $\text{Cs}_5\text{H}_3(\text{SO}_4)_4 \cdot x\text{H}_2\text{O}$ ($x \approx 0.5$) (PCHS) compound, which belongs to the family of proton conductors with a complex system of hydrogen bonds, is investigated by ^2H NMR spectroscopy. The temperature and orientation dependences of the ^2H NMR spectra are measured and analyzed. It is established that, upon transition to the glassy phase at the temperature $T_g = 260$ K, the parameters characterizing the proton exchange between positions in hydrogen bonds remain unchanged to within the limits of experimental error. The protons in the two-dimensional network of hydrogen bonds in the (001) plane are dynamically disordered over possible positions down to temperatures considerably lower than the glass transition point T_g . However, water molecules are fixed at particular structural positions in the phase transition range. In PCHS crystals with a nonstoichiometric water content, this circumstance can be responsible for the frustration that leads to the formation of the glassy state.

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1. INTRODUCTION

Crystals of the $\text{Cs}_5\text{H}_3(\text{SO}_4)_4 \cdot 0.5\text{H}_2\text{O}$ (PCHS) compound belong to a large family of compounds with the general formula $\text{Me}_z\text{H}_y(\text{AO}_4)_{(z+y)/2} \cdot x\text{H}_2\text{O}$ ($\text{Me} = \text{K}, \text{Rb}, \text{Cs}, \text{NH}_4; \text{A} = \text{S}, \text{Se}; 0 \leq x \leq 1$) [1, 2]. It is known that the high proton conductivity observed in superionic phases of representatives of this family is associated with the positional dynamic disordering of protons of hydrogen bonds. The representatives containing water can lose a considerable number of water molecules without changing the initial structure. Structures that are nonstoichiometric with respect to water ($x < 1$) retain a rather high proton conductivity upon supercooling to low temperatures [1, 3]. At temperatures below a specific point, there arise nonergodic glassy states, which are referred to as proton glass states [3, 4]. At present, the nature of these states is not clearly understood despite numerous investigations of their physical properties and structure [5–8].

It should be noted that the nature of the glassy state in $\text{Me}_z\text{H}_y(\text{AO}_4)_{(z+y)/2} \cdot x\text{H}_2\text{O}$ compounds differs from that in well-known proton glasses in mixed crystals belonging to the KDP family (see, for example, [5]).

The $\text{Cs}_5\text{H}_3(\text{SO}_4)_4 \cdot 0.5\text{H}_2\text{O}$ compound, which crystallizes in a hexagonal phase (space group $P6_3/mmc$) from an aqueous solution at room temperature, has been most extensively studied [9, 10]. According to the

x-ray diffraction [9, 10], neutron diffraction [11, 12], and Raman scattering [4, 13] data, the PCHS compound is characterized by a constant water content $x \approx 0.5$ and the symmetry of its structure remains unchanged in the temperature range from 20 to 414 K.

At high temperatures, the crystal structure is dynamically disordered over the orientational degrees of freedom of tetrahedral groups and over the positions of acidic protons of linear hydrogen bonds. A decrease in the temperature to liquid-helium temperatures does not lead to the transition to an ordered phase and a decrease in symmetry, as is the case with many other crystals of the $\text{Me}_z\text{H}_y(\text{AO}_4)_{(z+y)/2} \cdot x\text{H}_2\text{O}$ family. The PCHS compound undergoes a transition to the glassy state at a temperature $T_g \approx 260$ K [1, 3, 4]. Different assumptions have been made regarding the nature of this state in the literature. In particular, in the study of dielectric relaxation, the long-term α relaxation was attributed to frequency-dependent conduction that reflects the diffusion dynamics of acidic protons disordered in the hexagonal plane. It was revealed that the α relaxation is retarded at temperatures below the glass transition point T_g [3]. It is this ordering that was considered a factor responsible for the frustration of interactions at the temperature T_g in the Ising glass model [3]. More recently, vibrations of tetrahedral groups were investigated using electron paramagnetic resonance [14] and Raman scattering [4]. It was assumed that, in the transition range,

the orientational disordering of SO_4 ions and water molecules is "frozen" and becomes statistic; however, the hexagonal structure, on the whole, is retained. Moreover, the mobility of the protons of hydrogen bonds and their small displacements with respect to the midpoint of the O–O distance are also frozen. According to this interpretation, the glassy state in the PCHS structure is the orientational glass. However, the nature of the frustration of interactions is less clear than that within the interpretation proposed in [3].

It should be noted that vibrations of tetrahedral groups responsible for the formation of hydrogen bonds in the structure [9] should occur with a large amplitude. Freezing of these degrees of freedom in the transition range should lead to a change in the potential barriers hindering the diffusion. However, a linear temperature dependence of the static conductivity σ_0 in the $T^{-1}-\ln(\sigma_0 T)$ coordinates was observed over a wide temperature range, including the transition region [15]. Possibly, this dependence corresponds to some averaged parameters of the positional mobility of protons and does not reflect specific features of their change upon formation of the glassy state.

A more detailed information on the proton dynamics can be obtained using nuclear magnetic resonance as a direct investigation method. If isotopic substitution of deuterons for protons does not result in a change in the crystal structure [12], the proton dynamics and the system of hydrogen bonds can be thoroughly studied by the ^2H NMR technique. Unlike protons, deuterons possess an electric quadrupole moment. This makes it possible to observe well-resolved lines corresponding to different structural positions of protons. This approach was successfully used in our earlier works [16, 17] devoted to the study of proton exchange between different positions in crystals of the ammonium and potassium hydrogen selenates that belong to the aforementioned family. In the present work, the dynamics of protons of linear hydrogen bonds and H_2O molecules was investigated by the ^2H NMR method over a wide temperature range, including the transition to the proton glass phase.

2. SAMPLE PREPARATION AND EXPERIMENTAL TECHNIQUE

Partially deuterated (60% of the protons were replaced by deuterons) $\text{Cs}_5\text{H}_3(\text{SO}_4)_4 \cdot 0.5\text{H}_2\text{O}$ crystals were grown from an aqueous solution containing an appropriate amount of heavy water. The ^2H NMR spectra were measured on an AVANCE 300 NMR spectrometer operating at a Larmor frequency of 46.073 MHz. The width of a 90° pulse was equal to 4 μs . A spin echo sequence with a time interval of 20 μs between pulses was used to exclude the effect of the dead time of the NMR spectrometer receiver. Moreover, proton decoupling was employed to suppress the broadening of the ^2H NMR lines due to the dipole–dipole interaction with

the remaining protons. The ^2H NMR spectra of the PCHS compound were studied in the temperature range 180–340 K, which was determined by the operating temperatures of the spectrometer detector.

3. RESULTS AND THE SPECTRAL ASSIGNMENT

The crystal structure (taken from [9]) at room temperature is depicted in Fig. 1. The structural motif of the PCHS crystal is formed by layers of tetrahedra linked together by a complex system of hydrogen bonds. Three structurally nonequivalent hydrogen bonds O–H \cdots O designated as H(1), H(2), and H(3) at the 12*k*, 6*h*, and 24*l* crystallographic positions, respectively, are shown in the figure. It is assumed that the water molecules at the 2*c* positions are orientationally disordered.

According to the structural data for the PCHS crystal [9, 10], the deuterium nuclear magnetic resonance spectrum at low temperatures should exhibit a complex multicomponent structure, which consists of at least three doublets attributed to the three structurally nonequivalent linear hydrogen bonds and doublets corresponding to water molecules. For an arbitrary orientation when the direction of the magnetic field does not coincide with the symmetry axes, the number of lines further increases due to the appearance of magnetically nonequivalent positions. In this spectrum, pairs of lines should be assigned to specific structural positions of deuterons. In molecular groups (in our case, D_2O), the tensor of the electric-field gradient at deuterons is predominantly determined by the intramolecular contributions and is uniquely associated with the molecular geometry. For D_2O , the quadrupole coupling constants and the orientation of the principal axes of the tensor are known in the case of both a fixed water molecule and orientations with respect to local symmetry axes [18]. The spectrum of the deuterons of the linear hydrogen bonds linking neighboring SO_4 tetrahedra can also be identified by determining the electric-field gradient tensors. It is well known that the direction of the principal axis of the electric-field gradient tensor for the largest principal value V_{zz} approximately coincides with the direction of the hydrogen bond of this type and the maximum doublet splitting is approximately equal to 200 kHz.

We investigated the temperature dependences of the ^2H NMR spectra for the chosen crystal orientations in the magnetic field and the orientation dependences at a temperature of 220 K. The temperature dependence of the ^2H NMR spectrum for the crystal orientation at which the magnetic field lies in the (001) basal plane and makes an angle of 8° with the **a** axis is plotted in Fig. 2. The spectrum at a temperature of 340 K consists of one very narrow line at the Larmor frequency. The spectral shape indicates that the quadrupole interactions are completely averaged as a result of diffusive motion of protons in the system of hydrogen bonds of acidic protons and diffusion of water molecules over

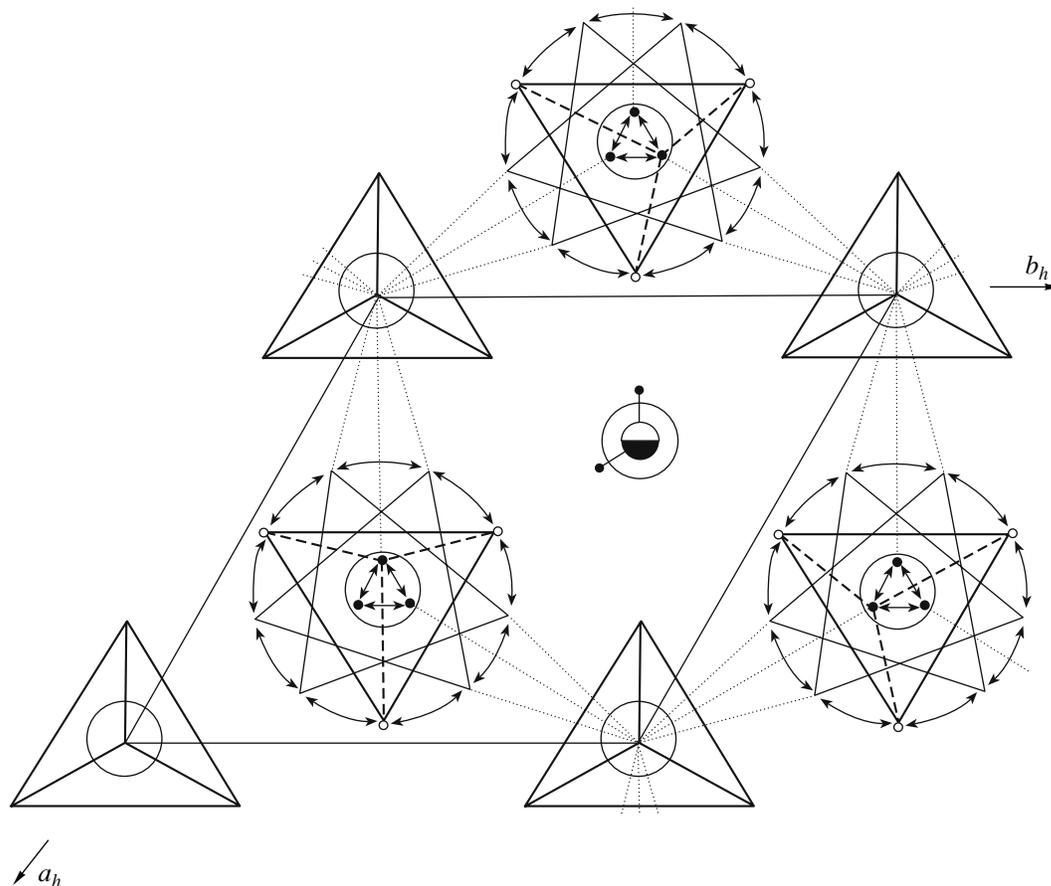


Fig. 1. Crystal structure of the hexagonal phase of the $\text{Cs}_5\text{H}_3(\text{SO}_4)_4 \cdot 0.5\text{H}_2\text{O}$ crystal in the projection onto the (001) plane [9]. Large open circles indicate the Cs atoms, the tetrahedra depicted by heavy lines represent the SO_4 groups, and the partially filled circle (at the center of the figure) is the H_2O molecule. Dotted lines between the tetrahedra show a dynamically disordered network of H(2) and H(3) hydrogen bonds, small open circles are the H(1) hydrogen bonds perpendicular to the (001) plane and linking the S(1) O_4 tetrahedra, small closed circles represent three equally probable positions of the vertices of the S(2) O_4 tetrahedron in the vicinity of the hexagonal axis (6_3), and arrows between them indicate librations of the S(2) O_4 tetrahedron. Arrows in the largest circles identify rotation of the tetrahedra. The tetrahedra depicted by thin lines show other possible orientations of the S(2) O_4 groups.

the equivalent positions in the lattice. It should be noted that, after heating to a temperature of 340 K, the external appearance of the crystal is changed and the spectrum recorded before heating incompletely regains its original shape. As was shown earlier in [14, 19], this circumstance is associated with the specific quasi-reversible structural transformations in the PCHS crystal on a mesoscopic scale at temperatures above 340 K. In this respect, the measurements in the temperature range 300–220 K (Fig. 2) were carried out using the sample that was not previously used in measurements. At a temperature of 300 K, the central line is broadened and takes the shape of a bell, which is characteristic of ^2H NMR spectra in the transition range where the correlation frequency of nuclear motion becomes of the order of quadrupole splittings of the doublets. Specific features are observed in the wings of the central line. As the temperature decreases, these specific features transform into doublet lines whose intensity increases and

the splitting does not depend on the temperature and is equal to 103 kHz. The formation of the doublet spectrum suggests that there is a proton subsystem in which the frequency of positional exchange is lower than the quadrupole splitting. At $T = 260$ K, three doublets with splittings of 42, 71, and 174 kHz appear against the background of the broad central component. These doublets are formed in a range of approximately 15 K in the vicinity of the transition point to the proton glass phase. A decrease in the temperature leads to the stabilization of the NMR spectrum, which, apart from the doublets, contains a very broad intense central component. The presence of this component indicates that there are protons with a high frequency of positional exchange at temperatures considerably lower than the glass transition point T_g .

In order to assign the doublets in the spectrum to specific types of the hydrogen bonds, we studied the

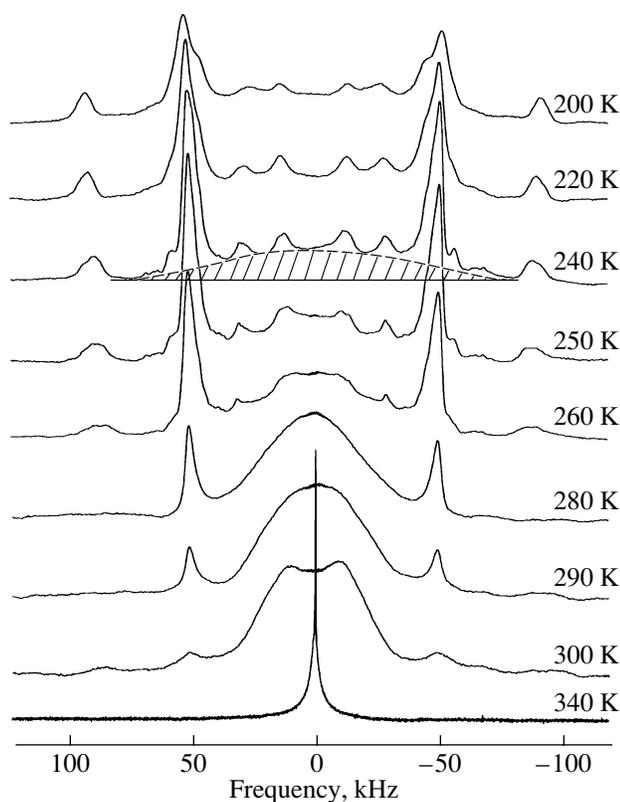


Fig. 2. Temperature dependences of the NMR spectra of the $\text{Cs}_5\text{H}_3(\text{SO}_4)_4 \cdot 0.5\text{H}_2\text{O}$ crystal. The external magnetic field H_0 is aligned with the (001) plane and makes an angle of 8° with the **a** axis. The hatched region corresponds to the broad line associated with the H(2) and H(3) protons.

orientation dependences of the quadrupole splitting

$$\nu_2 - \nu_1 = \frac{6eQ}{4h} V_{zz}^{\text{LAB}} = \Phi_{zz}, \quad (1)$$

where Q is the nuclear quadrupole moment, e is the elementary charge, h is the Planck constant, and V_{zz}^{LAB} is the z component (the field \mathbf{H}_0 is aligned along the z axis) of the tensor of the electric-field gradient at the nucleus. All the components V_{ij} of the electric-field gradient tensors for each structurally nonequivalent position of deuterons in the crystal structure in the laboratory coordinate system can be determined from the orientation dependences of the quadrupole splittings (1). For convenience of comparison with the experimental spectra, the quadrupole splittings Φ_{ij} expressed in terms of the frequency will be used rather than the electric-field gradient tensor components V_{ij} .

Upon rotation of the crystal about the **c** axis for all orientations of the magnetic field in the (001) plane, the splitting of the doublet appearing at temperatures below 300 K (Fig. 3a) is constant and equal to 103 kHz. Upon rotation about the **a** axis (Fig. 3b), the splitting varies as $3\cos^2\theta - 1$ and reaches a maximum value of 206 kHz at

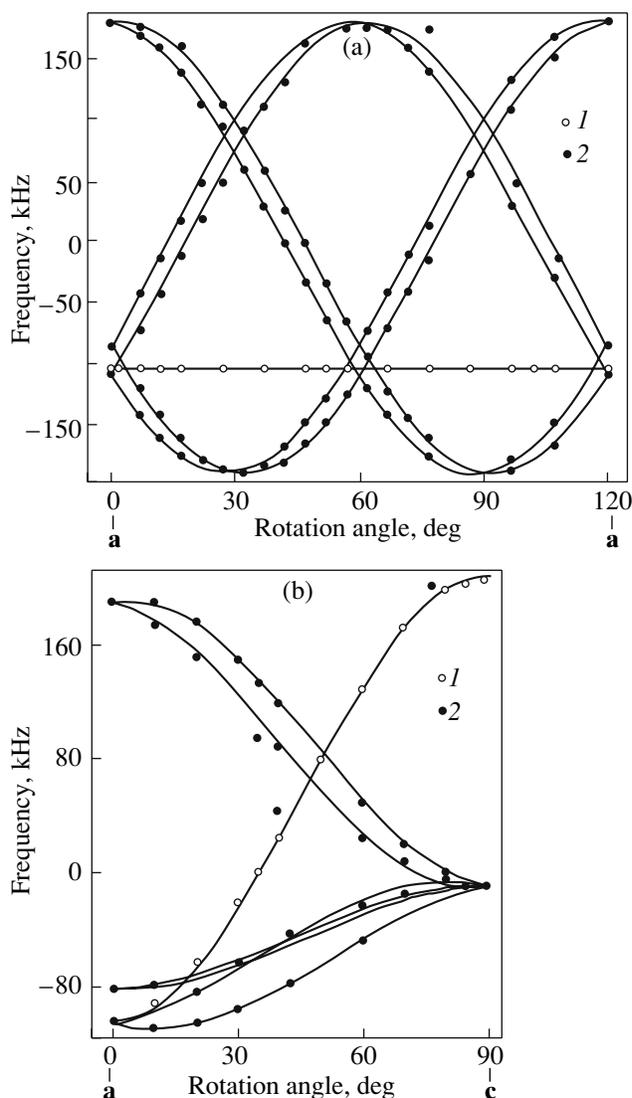


Fig. 3. Orientation dependences of the quadrupole splittings upon rotation of the crystal about (a) the **c** axis and (b) the **a** axis: (1) quadrupole splittings of the spectrum of deuterons at the H(1) position and (2) quadrupole splittings of the spectrum of deuterons in water molecules.

the orientation $\mathbf{H}_0 \parallel \mathbf{c}$. Consequently, the electric-field gradient tensor is axially symmetric and its principal axis is aligned along the **c** axis of the crystal (see table). In the structure (Fig. 1), this direction corresponds to the H(1) bond that is orthogonal to the basal plane. The electric-field gradient tensor with an asymmetry parameter close to unity and the principal value Φ_{zz} approximately equal to 200 kHz was determined from the orientation dependences of the quadrupole splittings of the doublets appearing in the range of the glass transition temperature T_g . This tensor is characteristic of water molecules flipping with the respect to the bisector of the D–O–D bond angle at a frequency substantially higher than the quadrupole splitting. Figure 3 shows the orientation dependences of the doublet splittings for

Parameters of the electric-field gradient tensors at $T = 220$ K for deuterons of H(1) hydrogen bonds and D₂O molecules in the Cs₅H₃(SO₄)₄ · 0.5H₂O crystal

H(1)				D ₂ O			
principal values of the electric-field gradient tensors Φ_{ii} , kHz	magnitudes of the direction cosines with respect to the crystallographic axes			principal values of the electric-field gradient tensors Φ_{ii} , kHz	magnitudes of the direction cosines with respect to the crystallographic axes		
	a	a*	c		a	a*	c
$\Phi_{xx} = -103$	1	0	0	$\Phi_{zz} = 190.8$	0.996	0.040	0.078
$\Phi_{yy} = -103$	0	1	0	$\Phi_{yy} = -180.6$	0.04	0.999	0.004
$\Phi_{zz} = 206$	0	0	1	$\Phi_{xx} = -10.2$	0.08	0.007	0.996

structurally equivalent D₂O molecules related by the 6₃ symmetry axis.

The directions of the principal axes of the electric-field gradient tensor (see table) determine the orientation of the water molecules with respect to the crystallographic axes. In particular, for the flipping water mol-

ecule, the component V_{zz} is perpendicular to the D–O–D plane, the component V_{yy} is parallel to the D–D direction, and the component V_{xx} is aligned with the bisector of the D–O–D angle [18]. The appearance of the doublets at temperatures in the vicinity of the glass transition point $T_g \approx 260$ K indicates the freezing of the diffusion of water molecules. The water molecule randomly occupies one of six equally probable positions in the hexagonal cell (space group $P6_3/mmc$).

In the spectrum (Fig. 2), the broad central component observed at temperatures below the glass transition point T_g is attributed to the H(2) and H(3) protons in the network of hydrogen bonds lying in the (001) plane. It can be seen from Fig. 2 that doublets with splittings of approximately 200 kHz for these bonds are not formed even at the lowest temperature of the measurement. Therefore, the frequency of diffusion motions in the (001) plane is considerably higher than the maximum quadrupole splitting. The NMR spectrum cannot be calculated in the transition range. However, the two-dimensional character of the proton mobility is clearly follows from the temperature dependence of the NMR spectra for the orientation $\mathbf{H}_0 \parallel \mathbf{c}$ (Fig. 4). For this orientation of the magnetic field, the doublet with a temperature-independent splitting of approximately 50 kHz and a small width of the components is assigned to the deuterons at the H(2) and H(3) positions. A decrease in the temperature leads to a gradual increase in the width of the components, i.e., a decrease in the exchange rate. However, no changes that indicate the freezing of the positional exchange between the H(2) and H(3) hydrogen bonds down to the lowest temperature are observed in the spectrum for the orientation $\mathbf{H}_0 \parallel \mathbf{c}$.

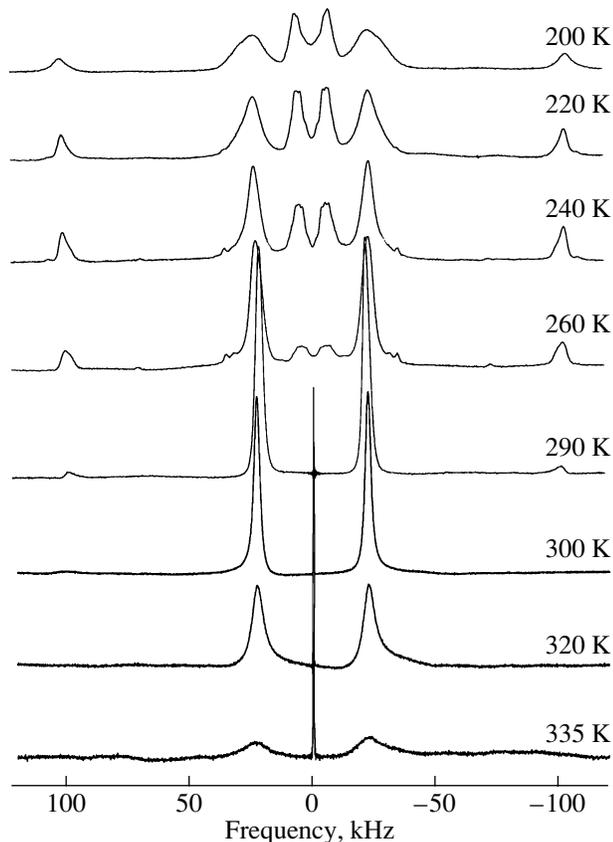


Fig. 4. Temperature dependences of the NMR spectra of the Cs₅H₃(SO₄)₄ · 0.5H₂O crystal in the external magnetic field $\mathbf{H}_0 \parallel \mathbf{c}$. The doublet spectrum with a splitting of 50 kHz is associated with the H(2) and H(3) protons. The doublet spectrum with a splitting of the order of 200 kHz is attributed to the H(1) protons. Lines of D₂O molecules appear in the central part of the spectra at temperatures in the vicinity of the glass transition point T_g .

4. DISCUSSION OF THE RESULTS

The coordinates of protons in crystals of the $Me_zH_y(AO_4)_{(z+y)/2} \cdot xH_2O$ family were not determined. The hypothetical model of the structure of bridging hydrogen bonds [9] is based on the assumption that these bonds are fluctuationally formed and broken in complex thermal motions of tetrahedral groups. As can be seen from Fig. 1, the structure involves tetrahedral

groups of two types, namely, the “fixed” $\text{S}(1)\text{O}_4$ and “mobile” $\text{S}(2)\text{O}_4$ groups. The latter groups cannot be only reoriented with respect to the 6_3 symmetry axis but also librate at a high amplitude with respect to the central ion. The $\text{H}(1)$ bond aligned with the \mathbf{c} axis is formed only in the case where mobile tetrahedra of neighboring layers occupy intermediate equilibrium positions with respect to the 6_3 axis (Fig. 1). The proton occupancy of this bond is equal to $1/3$. The $\text{H}(2)$ bond lying in the basal plane is formed between the vertex of the fixed tetrahedron and the vertex of the mobile tetrahedron librating with respect to the 6_3 axis. The occupancy of this bond is equal to $1/6$. The $\text{H}(3)$ bond can be formed only when the libration angle of the tetrahedron is close to 40° [9]. The occupancy of this bond lying approximately in the (001) plane is equal to $1/12$. It should be noted that the $\text{H}(2)$ and $\text{H}(3)$ bonds are formed when the tetrahedral groups involved in their formation are located at the extreme positions corresponding to the amplitudes of their vibrations.

The NMR data indicate that the PCHS crystal contains the proton subsystems in which the correlation times of positional exchange differ substantially. In particular, the proton exchange between the $\text{H}(1)$ hydrogen bond and the system of hydrogen bonds lying in the (001) plane is frozen on the NMR scale at temperatures considerably higher than the glass transition point T_g . The parameters of the electric-field gradient tensor remain virtually unchanged in the temperature range 300–180 K. This corresponds to the slow-motion limit. It is interesting to note that the electric-field gradient tensor given in the table for the $\text{H}(1)$ proton corresponds to the time-averaged proton position on the 6_3 axis rather than to the general positions related by this axis in the structure. This is possible only in the case of fast (on the NMR scale) reorientation of the $\text{S}(2)\text{O}_4$ tetrahedron with respect to the 6_3 axis. The electric-field gradient tensor presented in the table is retained down to the lowest temperature used in our measurements. According to the ^2H NMR data, the fast proton exchange between the positions in the hydrogen bonds in the basal plane is retained. The number of fluctuationally formed shallow minima in the potential relief is substantially larger than the number of protons participating in the exchange. This explains the high proton conductivity observed in the (001) plane in the proton glass phase. The data obtained are in agreement with strong anisotropy of the proton conductivity in the PCHS crystal: the conductivity along the \mathbf{c} axis in the crystal is almost two orders of magnitude lower than that in the perpendicular plane [1, 3].

The broadening of the central line in the ^2H NMR spectrum in Fig. 2 up to the disappearance in noises, as well as the broadening of the lines of the narrow doublet in Fig 4, is determined by the decrease in the frequency of the proton exchange between the positions in the hydrogen bonds lying in the basal plane with a decrease in the temperature. However, this process,

which is observed over a very wide range of temperatures, is not characterized by a critical retardation in the phase transition range. Therefore, the change in the temperature behavior of the long-term dielectric relaxation at temperatures in the vicinity of 240 K is not associated with the critical retardation of the diffusion dynamics of protons, as was proposed in [3]. No changes in the parameters of the diffusion motion of protons in the network of hydrogen bonds in the (001) plane occur in the transition range.

The doublets attributed to the water molecules fixed at possible equilibrium positions appear in the NMR spectrum in a narrow temperature range that coincides with the range of the transition to the glassy phase (Figs. 2, 3). A random location of H_2O molecules in approximately half the equilibrium positions related by the 6_3 axis leads to a structural inhomogeneity. Water molecules enter into the $\text{Cs}(1)$ and $\text{Cs}(2)$ coordination polyhedra. Therefore, the polyhedra with occupied and unoccupied H_2O vacancies differ from each other. Moreover, according to IR spectroscopy, weak hydrogen bonds formed by water molecules with different conglomerates of the $\text{H}-\text{SO}_4-\text{H}$ type stabilize these configurations in regions where water molecules are located [13]. Random freezing of water molecules in the case of a nonstoichiometric water content can be responsible for the frustration of interactions and the appearance of the glassy structure.

5. CONCLUSIONS

Thus, the inference can be made that, most likely, the occurrence of symmetry with space group $P6_3/mmc$ in the PCHS crystal down to low temperatures [10] is closely associated with the dynamic disordering of the structure of the glassy phase.

This is confirmed by the revealed reorientation of mobile tetrahedra with respect to the 6_3 axis at temperatures below the glass transition point T_g and by the absence of substantial changes in the parameters of proton diffusion in the basal plane upon transition according to the NMR data. It should be noted that the freezing of librations of mobile tetrahedra by angles close to 40° (the tetrahedra at the corresponding positions are depicted by the thin lines in Fig. 1) should lead to the loss of the 6_3 symmetry axis. It is not clear how this axis is restored as a hexagonal axis of the structure at temperatures below the glass transition point T_g . With due regard for the complex character of orientational mobility of tetrahedral groups, we can assume that the real mechanism of thermal vibrations can somewhat differ from the mechanism proposed in [9]. The transition to the glassy phase can lead to a change in the type of vibrations of tetrahedral groups rather than to a complete freezing of the orientational degrees of freedom. From this standpoint, it is of interest to determine experimentally the positions of the $\text{H}(2)$ and $\text{H}(3)$ hydrogen bonds by the NMR method and to establish

the averaging of the electric-field gradient tensors at the ^2H nuclei. For this purpose, it is necessary to perform measurements at temperatures below 130 K, i.e., at temperatures considerably lower than the operating temperatures of the standard detector of the spectrometer.

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