

## Investigation of hydrogen bond dynamics in $\text{NH}_4\text{IO}_3 \cdot 2\text{HIO}_3$ crystal by NQR

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The pressure dependence of the quadrupole coupling constant  $e^2Qq_{zz}$  and electric field gradient tensor asymmetry parameter  $\eta$  have been obtained from the analysis of  $^{127}\text{I}$  nuclear quadrupole resonance spectra at 77 K. It was shown that the phase transition mechanism in the crystal cannot be described as ordinary ordering of protons in bifurcated hydrogen bonds. The two-stage mechanism of the phase transition is discussed.

Барическая зависимость константы квадрупольного взаимодействия  $e^2Qq_{zz}$  и параметра асимметрии  $\eta$  тензора градиента электрического поля были получены из анализа спектров ядерного квадрупольного резонанса на ядрах  $^{127}\text{I}$  при 77 К. Показано, что механизм фазового перехода в кристалле не может быть описан как обычное упорядочение протонов бифурцированных водородных связей. Обсуждается двухступенчатый механизм фазового перехода.

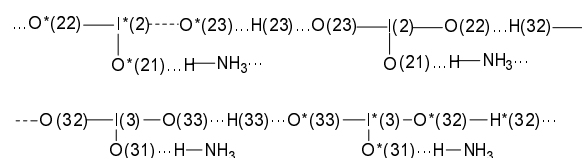
The  $\text{NH}_4\text{IO}_3 \cdot 2\text{HIO}_3$  crystal (AIH) is known as a proton conductor having a conductivity  $\rho$  of about  $10^{-6} \text{ Ohm}^{-1}\text{cm}^{-1}$  at room temperature. From the structural investigations of AIH crystal at 300 K [1–3], this crystal has been assigned to triclinic system ( $P = C_i^1$  space group with two formula units per unit cell  $Z = 2$ ). Basing on temperature dependence of dielectric permeability [1, 2], it was shown that at  $T_c = 213$  K, the crystal undergoes a second-order phase transition into superionic state. This superionic phase transition was assumed to be connected with the ordering of protons in short hydrogen bonds. According to this assumption, at  $T < T_c$  the crystal must take ferroelectric properties. However, temperature investigations of the crystal macroscale parameters show that the low-temperature phase of the crystal does not exhibit any polar properties [1]. Microscopic mechanisms of the phase transition in the AIH crystal were also studied in [4–6] by spectroscopic and DSC methods, where a two-stage mechanism of superionic conductivity in the crystals was proposed. However, this mechanism is not completely defined up to now. In this connection, this

work is aimed at elucidation of lattice dynamics and phase transition model for AIH crystal using nuclear quadrupole resonance (NQR) and vibrational spectroscopy experimental data.

The  $^{127}\text{I}$  NQR spectra of an AIH crystal were investigated at 77 K using an IS-3 pulsed quasi-coherent radiospectrometer. The measurement accuracy of the NQR line frequencies ( $\pm 10$  kHz) was provided by the determination accuracy of the quadrupole coupling constant  $e^2Qq_{zz}$  and electric field gradient tensor (EFGT) asymmetry parameter  $h\eta$  that were  $\pm 0.01$  MHz and 0.01 %, respectively. The pressure  $p \leq 4$  Kbar was provided using an autonomic high-pressure hydraulic cell. Transformer oil was used as the pressure transmitting medium. The homogeneity of hydrostatic pressure at 77 K was monitored using the  $^{127}\text{I}$  NQR line width in the NQR spectrum.

Basing on the neutron diffraction study [3], the AIH crystal structure and structure of  $\text{IO}_3$  iodate groups at 300 K were determined. The AIH crystal contains a framework of strongly distorted  $\text{IO}_6$  octahedrons linked together by bent hydrogen bonds. It

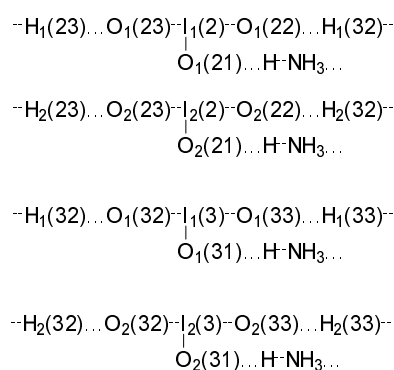
was found that different structure of distorted iodate groups  $I(1)O_3$ ,  $I(2)O_3$  and  $I(3)O_3$  is defined by their different local surrounding in the crystal. The  $NH_4^+$  ions occupy the large cavities in this framework. There are three types of the O—H...O bonds and four types of weak N—H...O bonds. Two oxygen atoms of  $I(1)O_3$  groups form two hydrogen bonds OH—N. A specific feature of the crystal structure is that  $I(2)O_3$  and  $I(3)O_3$  groups form infinite iodate chains which are connected with each other in transversal directions by weak OH—N bonds. The  $I(2)O_3$  and  $I(3)O_3$  groups are surrounded by one static OH—N bond and two disordered or bifurcated hydrogen bonds OHO. It was shown that the bifurcated hydrogen bonds are symmetric at 300 K. The structure fragments formed by iodate chains in the crystal at 300 K may be presented as follows:



According to [2], another specific feature of the AIH crystal structure at room temperature is that the number of possible sites for protons localization in the lattice exceeds the number of protons per unit cell. This fact is responsible for the superionic conductivity mechanism in the crystal observed at temperatures exceeding 213 K. The existence of three kinds of iodate groups at 300 K should result in the multiplicity of the  $^{127}I$  NQR spectrum, namely, the NQR spectrum should consist of three lines. As it follows from the analysis of the crystal symmetry, the  $^{127}I$  NQR spectrum at 77 K (at  $T < T_c$ ) must be transformed into that consisting of six lines [7]. The assignment of these six  $^{127}I$  NQR lines observed for the AIH crystal at 77 K (Table 1) has

been made only using additional experimental data, namely, using the analysis of baric coefficients for the experimental  $e^2Qq_z(p)$  and  $\eta(p)$  dependences.

The observed NQR spectrum multiplicity can be explained by breakdown of bifurcated hydrogen bonds which became asymmetric at  $T = T_c$ . In this case (at  $T < T_c$ ), each of the three NQR lines observed at 300 K becomes split into two lines and, therefore, the NQR spectrum at 77 K consists of six lines. This assumption agrees with the supposed iodate chain structure in the AIH crystal at 77 K, when the protons may occupy the asymmetric positions on bifurcated hydrogen bonds. The structures of the chains with ordered protons can be presented as follows:



The NQR lines were assigned by comparing the pressure coefficients  $(1/q_{zz}^0)(dq_{zz}/dp)$  and  $(1/\eta^0)(d\eta/dp)$  of the  $e^2Qq_{zz}(p)$  and  $\eta(p)$  dependences obtained for different iodate crystals of well-studied crystal structure (See Table 2). The asymmetry parameter of electric field gradient  $h\eta$  and the quadrupole coupling constant  $e^2Qq_{zz}$  for different lines of multiple NQR spectra at various values of hydrostatic pressure were determined using the tables from [7].

Since the AIH crystal symmetry centers at 300 K lay at geometrical centers of bifurcated hydrogen bonds [2], the assumed model of the phase transition must result in

Table 1. Parameters of  $^{127}I$  NQR spectra of  $NH_4IO_3 \cdot 2H_2O$  crystal at 77 K

	$\nu_{1/2-3/2}$ , MHz	$\nu_{3/2-5/2}$ , MHz	$e^2Qq_{zz}$ , MHz	$\eta$ , %
1	156.25	309.46	1033.12	8.70
2	157.05	312.65	1042.93	5.98
3	159.32	309.53	1036.51	15.12
4	180.41	330.62	1117.66	26.92
5	173.78	318.63	1077.25	26.83
6	202.24	320.15	1109.71	46.86

Table 2. Pressure coefficients of  $e^2Qq_{zz}(p)$  and  $\eta(p)$  dependences for  $\text{NH}_4\text{IO}_3 \cdot 2\text{HIO}_3$  crystal and assignment of NQR lines at 77 K

	$e^2Qq_{zz}$ , MHz	$\eta$ , %	$(1/q_{zz}^0)(dq_{zz}/dp)$ $10^3$ , kbar $^{-1}$	$(1/\eta^0)(d\eta/dp)$ $10^3$ , kbar $^{-1}$	Assignment
1	1033.12	8.70	0.9	16.2	...H-N $l_{1,2}(1)\text{O}_3$
2	1042.93	5.89	0.9	14.6	...H-N
3	1036.51	15.12	1.1	13.0	...H-N $l_1(2)\text{O}_3$ ...H-O ...H-O
4	1117.66	26.92	–	–	–H...O $l_2(2)\text{O}_3$ ...H-O ...H-N
5	1077.25	26.83	–0.2	–9.9	–H...O $l_1(3)\text{O}_3$ ...H-O ...H-O
6	1109.71	46.86	1.0	0.2	–H...O $l_2(3)\text{O}_3$ –H... O ...H-N

loss of the symmetry centers at 77 K. However, as we have already noted, no ferroelectric properties were detected for AIH crystal at 77 K: neither domain structure of the crystal no hysteresis loops were observed [1]. These experimental facts can be explained by the arising of antipolarity in the crystal structure at  $T < T_c$  and by doubling of the crystal unit cell with the symmetry of the crystal as a whole remaining unchanged. In this case, the crystal symmetry centers move from centers of bifurcated hydrogen bonds into another positions which join two hydrogen bonds of the same ordering with opposite (antipolar) proton locations. The phase transition scheme can be written as:

$$C_i^l(Z = 2) \xrightarrow{T_c} 2[C_1(Z = 2)] \equiv C_i^l(Z = 4).$$

However, the proposed phase transition mechanism in AIH needs a further verifica-

tion, e.g., using analysis of the crystal vibrational spectra in the phase transition temperature range.

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## **Дослідження динаміки водневих зв'язків у кристалі $\text{NH}_4\text{IO}_3 \cdot 2\text{HIO}_3$ методом ЯКР**

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Барична залежність константи квадрупольної взаємодії  $e^2Qq_{zz}$  та параметра асиметрії і тензора градієнта електричного поля було одержано з аналізу спектрів ядерного квадрупольного резонансу на ядрах  $^{127}\text{I}$  при 77 К. Показано, що механізм фазового переходу в кристалі не може бути описаний як звичайне упорядкування протонів біфуркованих водневих зв'язків. Обговорюється двоступінчастий механізм фазового переходу.