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X-RAY AND NEUTRON SINGLE CRYSTAL DIFFRACTION ON $(NH_4)_3H(SO_4)_2$.
II. REFINEMENT OF CRYSTAL STRUCTURE OF PHASE II AT ROOM TEMPERATURE

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Рентгеновская и нейтронная монокристальная дифракция на $(NH_4)_3H(SO_4)_2$.
II. Уточнение кристаллической структуры фазы II при комнатной температуре

Соединение $(NH_4)_3H(SO_4)_2$ привлекает особый интерес в связи с возможным влиянием ионов аммония на последовательность фазовых переходов: I $\Rightarrow$ II $\Rightarrow$ III $\Rightarrow$ IV $\Rightarrow$ V $\Rightarrow$ VII.

Предыдущее рентгеновское монокристальное дифракционное исследование фазы II в $(NH_4)_3H(SO_4)_2$ показало, что кристаллическая структура этого соединения состоит из двух кристаллографически независимых групп ионов аммония $NH_4(1)$ и $NH_4(2)$, но ориентационные положения этих ионов аммония не были определены точно.

Уточнение ориентационных позиций $NH_4(1)$ и $NH_4(2)$ в фазе II проведено с помощью рентгеновского и нейтронного монокристального дифракционного исследования. Анализ дифференциальных фурье-карт электронной зарядовой плотности и ядерной плотности указывает на возможность разупорядочения ионов аммония $NH_4(2)$.

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X-Ray and Neutron Single Crystal Diffraction on $(NH_4)_3H(SO_4)_2$.
II. Refinement of Crystal Structure of Phase II at Room Temperature

The $(NH_4)_3H(SO_4)_2$ is of special interest due to the possible influence of ammonium ions on the series of phase transitions: I $\Rightarrow$ II $\Rightarrow$ III $\Rightarrow$ IV $\Rightarrow$ V $\Rightarrow$ VII.

Earlier, the X-ray single crystal diffraction study of phase II of $(NH_4)_3H(SO_4)_2$ showed that the crystal structure of this compound has two crystallographically independent groups of ammonium ions $NH_4(1)$ and $NH_4(2)$, but orientational positions of these ammonium ions were not determined exactly.

The refinement of $NH_4(1)$ and $NH_4(2)$ orientational positions in phase II is carried out with the help of the X-ray and neutron single crystal diffraction study. The analyses of differential Fourier maps of electron charge density and nuclear density point out the possibility of disordering of $NH_4(2)$ ammonium ions.

The investigation has been performed at the Frank Laboratory of Neutron Physics, JINR.

INTRODUCTION

The compounds of the $Me_3H(SO_4)_2$ (Me = Na, K, Rb, Cs and NH_4^+) type are of interest because they have a high temperature phase with superionic conductivity. However, it is known that with lowering of temperature only $(NH_4)_3H(SO_4)_2$ undergoes a series of structural phase transitions at ambient pressure [1–3]. The temperatures of phase transitions are presented below:

Phase I$\Rightarrow$413 K$\Rightarrow$II$\Rightarrow$265 K$\Rightarrow$III$\Rightarrow$139 K$\Rightarrow$IV$\Rightarrow$133 K$\Rightarrow$V$\Rightarrow$63 K$\Rightarrow$VII

The X-ray structure investigations have been done for phases I [3–5], II [6–8], III [8, 9], IV [8, 10] and V [8]. The recent X-ray single crystal diffraction study of the crystal structure of $(NH_4)_3H(SO_4)_2$ in phase II, carried out at room temperature in [8], confirmed the earlier determined monoclinic syngony of this phase with space group (sp. gr.) $C2/c$, $Z = 4$, and with lattice parameters $a = 15.390(3)$ Å, $b = 5.848(1)$ Å, $c = 10.140(2)$ Å, $\beta = 101.81(3)°$. Sulfate ions are linked in dimers by hydrogen bonds O–H$\cdots$O via acid hydrogen. It was shown that this acid hydrogen is distributed between double potential minima with equal 50% occupation. Ammonium ions $NH_4(1)$ and $NH_4(2)$ occupy two sets of crystallographically non-equivalent positions: eight $NH_4(1)$ ions in general positions and four $NH_4(2)$ ions in special positions on the two-fold axis of the unit cell. The N–H distances determined by the X-ray single crystal diffraction lie from 0.78 to 1.02 Å, as determined in [6], and from 0.79 to 0.91 Å, as determined in [7]. Such a difference in hydrogen bond lengths of N–H(i) ($i = 1,\ldots 4$) led to the conclusion that the geometrical shape of NH_4^+ ions differs from a regular tetrahedron.

The X-ray single crystal diffraction study of [8] was dedicated to the refinements of crystal structures of phases II, III and IV and the determination of crystal structure of phase V in $(NH_4)_3H(SO_4)_2$. The authors of this investigation generally studied the behavior of sulfate ions, which form an isolated dimer via a strong ionic $O^-–H^+ \cdots O^-$ hydrogen bond and participate in a network of $N^+–H \cdots O^-$ hydrogen bonds in phases II, III, IV and V.

More attention to the behavior of ammonium ions in phase II of $(NH_4)_3H(SO_4)_2$ was given in [6], where authors pointed out the role of N–H$\cdots$O hydrogen bonds of both $NH_4(1)$ and $NH_4(2)$ groups, which could influence the reorientation or statistical order of these ammonium ions.

The information about ammonium groups of triammonium hydrogen disulphate in phase II was obtained by the X-ray single crystal diffraction study of $(ND_4)_3H(SO_4)_2$ in [11]. The N–D bonds for $ND_4(1)$ and $ND_4(2)$ ammonium groups were determined within the limits from 0.70 to 0.81 Å.

The recent investigation of the $[Rb_{0.11}(NH_4)_{0.89}]_3H(SO_4)_2$ mixed crystal, carried out by the X-ray and neutron single crystal diffraction, showed that N–H hydrogen bonds of ammonium groups, determined by neutron diffraction, are larger than those, determined by X-ray diffraction, and are more suited to regular tetrahedron [12]. Phase II in the $[Rb_{0.11}(NH_4)_{0.89}]_3H(SO_4)_2$ mixed crystal exists until 30 K, below which this mixed crystal transforms to orientational glass in accordance with the x–T phase diagram [13]. It was shown in [12, 14], that in phase II of $[Rb_x(NH_4)_{1-x}]_3H(SO_4)_2$ mixed crystal with $x = 0.18$ the quasielastic incoherent neutron scattering (QINS) is observed with cooling down to 150 K. The observation of QINS correlates with the detection of electron density and nuclear density of additional maxima on differential Fourier maps near $NH_4(1)$ and $NH_4(2)$ groups [12].

The recent investigation is devoted to the complex X-ray and neutron single crystal diffraction study of phase II in $(NH_4)_3H(SO_4)_2$ to determine N–H hydrogen bonds for $NH_4(1)$ and $NH_4(2)$ ammonium groups and differential Fourier maps for these ammonium ions by different diffraction methods.

EXPERIMENTAL RESULTS

The single crystal of $(NH_4)_3H(SO_4)_2$ was grown from water solution at ambient temperature at the Institute of Crystallography of RAS.

The X-ray single crystal diffraction measurements have been performed at room temperature using the Kuma4CCD X-ray diffractometer (Warsaw University, Chemistry Department, Warsaw, Poland) [8] and neutron single crystal diffraction measurements have been carried out at room temperature on the E5 neutron four-circle diffractometer of the BER-2 reactor of BENSC HMI (Berlin, Germany) [15].

The treatment of experimental X-ray and neutron data is carried out by programs [16, 17]. The conditions of the measurements including the used wavelengths, the refined space group, the obtained lattice parameters, the number of measured reflections, the number of unique reflections for the refinement of atomic positions and the R-factors of refinement are presented in Table 1.

Table 1. Crystal data and structure refinement of $(NH_4)_3H(SO_4)_2$ at 300 K (single crystal neutron and X-ray diffraction)

Phase II		
Radiation	Neutron	X-ray
T, K	300	300
Wavelength, E	0.914	0.71073
Crystal syngony, space group, Z	Monoclinic, $C2/c$, 4	Monoclinic, $C2/c$, 4
Unit cell dimensions		
a	15.435(2) E	15.390(3) E
b	5.8647(12) E	5.8480(12) E
c	10.170(3) E	10.140(2) E
α	90°	90°
β	101.83(3)°	101.81(3)°.
γ	90°	90°
Theta range for data collection	6.83–46.16°	3.74–28.80°
Limiting indices	$-24 \leqslant h \leqslant 23,$ $-8 \leqslant k \leqslant 0,$ $-9 \leqslant l \leqslant 15$	$-20 <= h <= 20,$ $-7 <= k <= 7,$ $-13 <= l <= 13$
Reflections collected/unique	1828 / 1596 [R(int) = 0.2571]	7795 / 1115 [R(int) = 0.0390]
Refinement method	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2
Data/restraints/ /parameters	1596 / 0 / 102	1115 / 0 / 86
Goodness-of-fit on F^2	2.07	1.120
Final R indices [I > 2sigma(I)]	R1 = 0.2019, wR2 = 0.5351	R1 = 0.0369, wR2 = 0.0900
R indices (all data)	R1 = 0.2808, wR2 = 0.5876	R1 = 0.0434, wR2 = 0.0957
Extinction coefficient	0.45(10)	0.068(4)
Largest differential peak and hole	2.983 and -3.945 e.E^{-3}	0.484 and -0.514 e.A^{-3}

  The determined atomic positions and U(eq) equivalent isotropic displacement parameters for $(NH_4)_3H(SO_4)_2$ at 300 K, sp. gr. $C2/c$, by means of the neutron and X-ray diffraction are presented in Tables $2a$ and $2b$, respectively. The U(eq) is defined as one third of the trace of the orthogonalized Uij tensor.

Table 2a. **(NH$_4$)$_3$H(SO$_4$)$_2$, T = 300 K, sp. gr.** *C2/c*. **Atomic coordinates (× 10^4) and U(eq) equivalent isotropic displacement parameters (Å^2 × 10^3) for 300 K; U(eq) is defined as one third of the trace of the orthogonalized Uij tensor (neutron diffraction)**

Atom	x	y	z	U(eq)
S	1164(5)	2514(16)	9476(9)	24(2)
O1	156(4)	2461(17)	8909((11)	69(3)
O2	1384(6)	2494(15)	1.0966(6)	52(2)
O3	1461(5)	4541(12)	8931(8)	48(2)
O4	1495(4)	473(12)	8962(8)	44(2)
N1	3002(2)	7499(7)	8529(3)	33(1)
N2	5000	2529(8)	7500	25(1)
H1	3170(22)	8787(42)	9035(36)	131(11)
H2	2326(12)	7590(57)	8415(31)	131(12)
H3	3166(14)	7490(53)	7743(18)	110(9)
H4	3121(20)	6126(32)	8922(33)	118(9)
H1O	−661(64)	995(156)	9579(97)	

Table 2b. **(NH$_4$)$_3$H(SO$_4$)$_2$, T = 300 K, sp. gr.** *C2/c*. **Atomic coordinates (× 10^4) and U(eq) equivalent isotropic displacement parameters (Å^2 × 10^3) for** *C2/c*; **U(eq) is defined as one third of the trace of the orthogonalized Uij tensor (X-ray diffraction)**

Atom	x	y	z	U(eq)
S	1141(1)	2184(1)	9614(1)	28(1)
O1	145(1)	1852(3)	9426(2)	44(1)
O2	1503(1)	2232(3)	11053(2)	44(1)
O3	1291(1)	4330(3)	8984(2)	48(1)
O4	1488(1)	270(3)	8980(2)	47(1)
N1	3011(2)	7759(4)	8473(2)	38(1)
N2	5000	2303(5)	7500	33(1)
H1	3220(40)	8610(100)	8970(60)	130(20)
H2	2460(30)	8070(70)	8490(40)	92(13)
H3	3170(30)	7840(70)	7880(60)	95(16)
H4	3050(30)	6450(80)	8790(40)	97(14)
H5	4660(30)	2940(70)	7720(50)	110(18)
H6	4740(30)	1570(80)	6930(40)	101(15)
H1O	0	0	10000	160(30)

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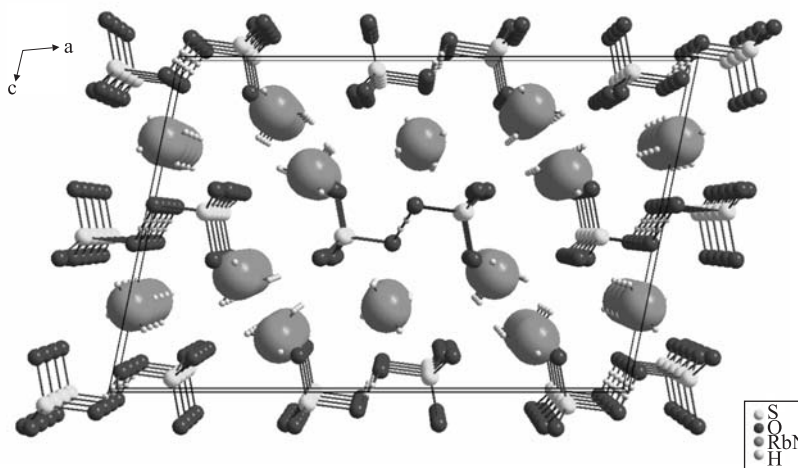
Fig. 1. The projection of $(NH_4)_3H(SO_4)_2$ (room temperature, *C2/c* sp. gr.) along the Y-axis – direction (010)

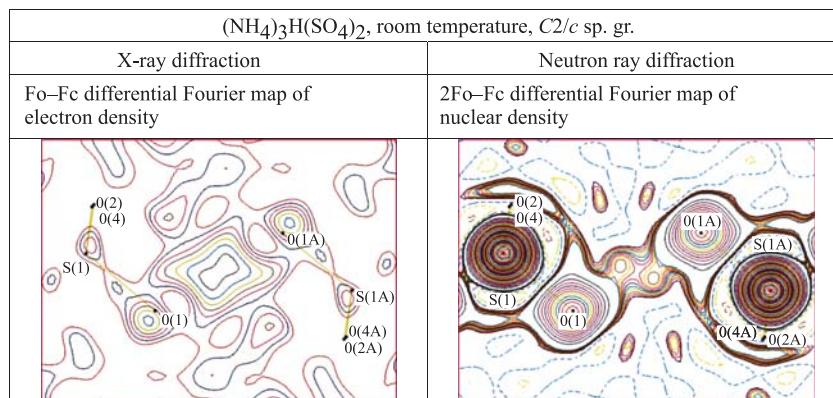| $(NH_4)_3H(SO_4)_2$, room temperature, *C2/c* sp. gr.	
X-ray diffraction	Neutron ray diffraction
Fo–Fc differential Fourier map of electron density	2Fo–Fc differential Fourier map of nuclear density

Fig. 2. The Fo–Fc and 2Fo–Fc differential Fourier maps of electron and nuclear densities in the region of H(1O) along S(1)O(1)H(1O)O(1A)S(1A) hydrogen bond

The projection of phase II of crystal structure of $(NH_4)_3H(SO_4)_2$ on the (010) plane is presented in Fig. 1. One can see, that the acid H(1O) hydrogen occupies minima in a double-well potential. Detailed positions of the acid H(1O) hydrogen are presented with the help of Fo–Fc and 2Fo–Fc differential Fourier maps of electron and nuclear densities in Fig. 2.

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The anisotropic displacement parameters Uij for $(NH_4)_3H(SO_4)_2$ in phase II at room temperature, determined by the neutron and X-ray diffraction, are presented in Tables 3a and 3b, respectively.

Table 3a. $(NH_4)_3H(SO_4)_2$, T = 300 K, sp. gr. *C2/c*. Anisotropic displacement parameters ($\text{Å}^2 \times 10^3$) for 300 K (neutron diffraction)

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
S	16(3)	15(3)	40(4)	–27(4)	2(3)	13(3)
O1	16(4)	65(5)	123(7)	–3(6)	–0(3)	2(3)
O2	72(4)	50(4)	42(3)	4(3)	30(3)4(4)	52(2)
O3	60(4)	26(3)	60(5)	16(3)	15(3)	–9(3)
O4	37(3)	32(3)	63(4)	–23(3)	14(3)	4(2)
N1	36(2)	20(2)	46(2)	2(1)	14(1)	6(1)
N2	24(2)	16(2)	37(2)	0	8(1)	0
H1	163(25)	59(12)	188(27)	–58(16)	77(21)	–55(15)
H2	44(8)	184(35)	172(22)	–56(21)	38(11)	–8(14)
H3	80(11)	188(28)	70(9)	39(14)	32(8)	46(14)
H4	164(23)	28(7)	179(24)	27(11)	71(19)	20(10)
H1O	172(27)					

Table 3b. $(NH_4)_3H(SO_4)_2$, T = 300 K, sp. gr. *C2/c*. Anisotropic displacement parameters ($\text{Å}^2 \times 10^3$) for *C2/c* (X-ray diffraction)

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
S	29(1)	29(1)	28(1)	0(1)	6(1)	3(1)
O1	25(1)	56(1)	49(1)	–1(1)	5(1)	2(1)
O2	41(1)	63(1)	27(1)	2(1)	2(1)	–7(1)
O3	50(1)	36(1)	55(1)	17(1)	6(1)	2(1)
O4	44(1)	39(1)	63(1)	–18(1)	20(1)	0(1)
N1	46(1)	35(1)	35(1)	1(1)	11(1)	7(1)
N2	35(1)	37(1)	28(1)	0	6(1)	0

Bond lengths (Å) and angles (degrees) for $(NH_4)_3H(SO_4)_2$ in phase II at room temperature, determined by the neutron and X-ray diffraction, are presented in Tables 4a and 4b, respectively.

Table 4*a*. Bond lengths (Å) and angles (degrees) for 300 K (neutron data)

S(1)–O(3)	1.436(11)
S(1)–O(4)	1.450(8)
S(1)–O(2)	1.478(11)
S(1)–O(1)	1.540(11)
N(2)–H(4)	0.891(15)
N(2)–H(7)	0.893(19)
N(2)–H(5)	0.923(16)
N(2)–H(6)	1.017(18)
O(1)–H(1)	1.428(13)
O(3)–S(1)–O(4)	112.2(7)
O(3)–S(1)–O(2)	111.9(7)
O(4)–S(1)–O(2)	111.0(7)
O(3)–S(1)–O(1)	104.8(7)
O(4)–S(1)–O(1)	104.8(6)
O(2)–S(1)–O(1)	111.9(8)
H(4)–N(2)–H(6)	112(3)
H(7)–N(2)–H(6)	106(3)
H(5)–N(2)–H(6)	99(3)

Table 4*b*. Bond lengths (Å) and angles (degrees) for $C2/c$ (X-ray diffraction)

Atoms	Bond lengths (Å)	Atoms	Angles (degrees)
S–O4	1.4456(15)	O4–S–O3	111.65(11)
S–O3	1.4478(16)	O4–S–O2	111.19(11)
S–O2	1.4521(16)	O3–S–O2	111.32(10)
S–O1	1.5191(16)	O4–S–O1	107.49(10)
O1–H1O	1.2702(18)	O3–S–O1	107.65(10)
N1–H1	0.73(6)	O2–S–O1	107.30(10)
N1–H2	0.87(5)	S–O1–H1O	108.60(11)
N1–H3	0.70(6)	H1–N1–H2	98(5)
N1–H4	0.83(5)	H1–N1–H3	111(5)
N2–H5	0.71(5)	H2–N1–H3	121(5)
N2–H6	0.76(4)	H1–N1–H4	112(5)
		H2–N1–H4	101(4)
		H3–N1–H4	113(4)
		H5–N2–H6	103(6)

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The Fo–Fc differential Fourier maps of electron and nuclear densities near $NH_4(1)$ and $NH_4(2)$ groups of $(NH_4)_3H(SO_4)_2$ at room temperature in phase II are presented in Figs. 3 and 4, respectively.

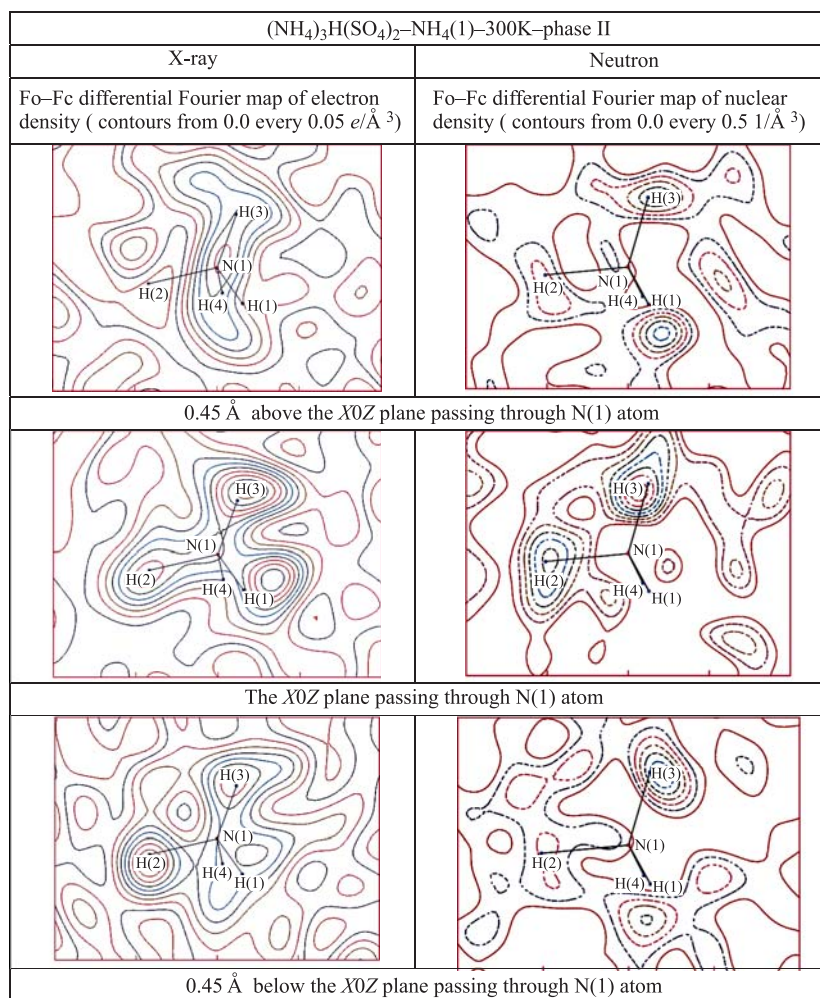| $(NH_4)_3H(SO_4)_2$–$NH_4(1)$–300K–phase II	
X-ray	Neutron
Fo–Fc differential Fourier map of electron density (contours from 0.0 every 0.05 e/Å ^{3})	Fo–Fc differential Fourier map of nuclear density (contours from 0.0 every 0.5 1/Å ^{3})
0.45 Å above the $X0Z$ plane passing through N(1) atom	
The $X0Z$ plane passing through N(1) atom	
0.45 Å below the $X0Z$ plane passing through N(1) atom	

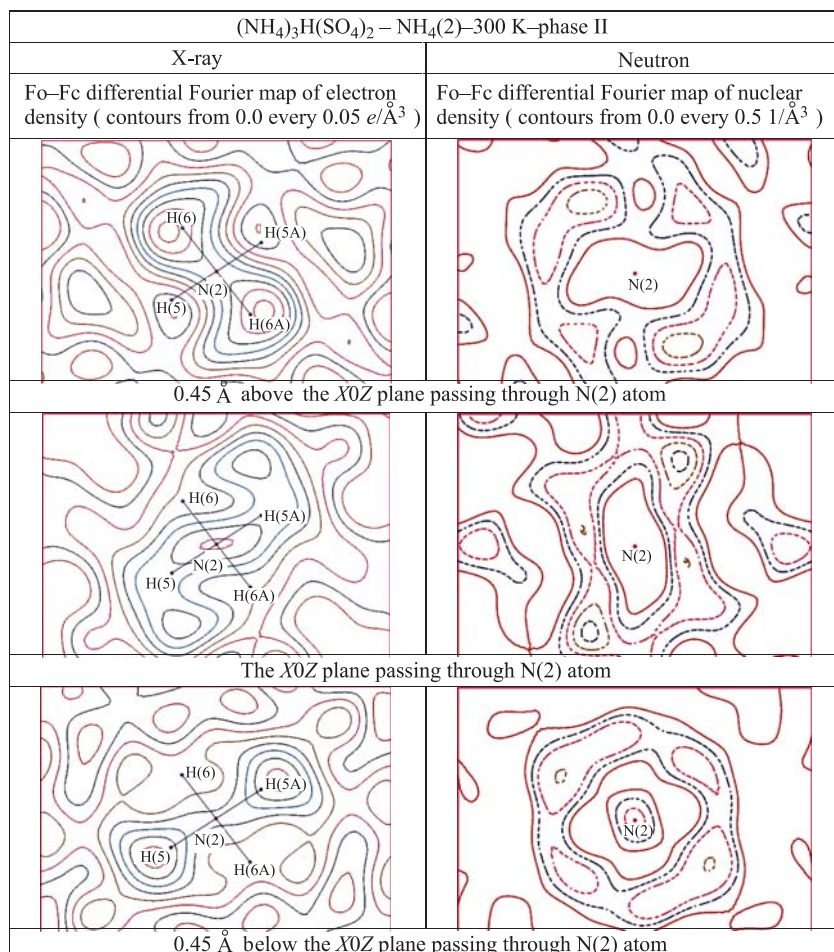Fig. 3. The Fo–Fc differential Fourier maps of electron and nuclear densities near N(1) atom of $(NH_4)_3H(SO_4)_2$

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(NH$_4$)$_3$H(SO$_4$)$_2$ – NH$_4$(2)–300 K–phase II	
X-ray	Neutron
Fo–Fc differential Fourier map of electron density (contours from 0.0 every 0.05 e/Å^3)	Fo–Fc differential Fourier map of nuclear density (contours from 0.0 every 0.5 1/Å^3)

0.45 Å above the X0Z plane passing through N(2) atom

The X0Z plane passing through N(2) atom

0.45 Å below the X0Z plane passing through N(2) atom

Fig. 4. The Fo–Fc differential Fourier maps of electron and nuclear densities near N(2) atom of (NH$_4$)$_3$H(SO$_4$)$_2$

CONCLUSIONS

The analyses of refinement results determined by the X-ray and neutron single crystal diffraction for (NH$_4$)$_3$H(SO$_4$)$_2$ show that R-factor for experimental data obtained by the X-ray single crystal diffraction corresponds to more reliable values of parameters of crystal structure of phase II. Insufficient R-factor for experimental data obtained by neutron single crystal diffraction was the cause of

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the presentation of neutron diffraction results with the help of Fo–Fc differential Fourier maps of nuclear density and the comparison with Fo–Fc differential Fourier maps of electronic density of ammonium ions.

The obtained N–H hydrogen bonds for ammonium groups by X-ray diffraction lie within the limits from 0.70 to 0.87 Å and an average N–H hydrogen bond equals 0.77 Å. The obtained N–H hydrogen bonds for ammonium groups by neutron diffraction lie within the limits from 0.89 to 1.02 Å and an average N–H hydrogen bond equals 0.931 Å. The limits for N–H hydrogen bonds from neutron diffraction are close to similar limits from X-ray diffraction and such neutron results do not give the possibility to confirm that the geometrical form of ammonium ions may be considered as a regular tetrahedron. However, the average value of N–H hydrogen bond 0.931 Å, determined by neutron diffraction, is higher than that of N–H hydrogen bond 0.77 Å, determined by X-ray diffraction, and is close to the average value 0.947 Å, obtained for ammonium ions in phase II for the $[Rb_{0.11}(NH_4)_{0.89}]_3H(SO_4)_2$ mixed crystal [12].

The contouring of Fo–Fc differential Fourier maps of electronic and nuclear densities of $NH_4(1)$ and $NH_4(2)$ ammonium ions gives the possibility to do the visualization of their orientational positions. If it is difficult to find the correspondence between electronic densities and nuclear densities for $NH_4(1)$ ammonium ion at different positions in relation to the $X0Z$ plane then it is easy to find the correspondence between electronic densities and nuclear densities for $NH_4(2)$ ammonium ion at different positions in relation to the $X0Z$ plane. So, in electronic densities one can see clear positions of H(6) and H(6A) hydrogen atoms above the $X0Z$ plane passing through the N(2) atom at 0.45 Å and clear positions of H(5) and H(5A) hydrogen atoms below the $X0Z$ plane passing through the N(2) atom at 0.45 Å.

In nuclear densities one can also see clear positions of H(6) and H(6A) hydrogen atoms above the $X0Z$ plane passing through the N(2) atom at 0.45 Å and clear positions of H(5) and H(5A) hydrogen atoms below the $X0Z$ plane passing through the N(2) atom at 0.45 Å. However, the nuclear density near the N(2) atom is more complex in comparison with the respective electronic density near this atom. The nuclear density above and below the $X0Z$ plane passing through the N(2) atom at 0.45 Å can be presented by a toroid with six various positions. The $NH_4(2)$ ammonium ion can occupy these positions describing phase II in $(NH_4)_3H(SO_4)_2$ as a disordered one.

The possibility of disordering of ammonium ion availability in phase II of $(NH_4)_3H(SO_4)_2$ can be confirmed by the presence of quasielastic incoherent neutron scattering contribution to inelastic incoherent neutron scattering spectra on the wings of the elastic lines from crystals-monochromators at the wavelength of 4.15 Å as it is observed on the corresponding spectra from $(NH_4)_3H(SO_4)_2$, presented in Fig. 5. The presented inelastic incoherent neutron scattering from $(NH_4)_3H(SO_4)_2$ is measured at 290 K (phase II), 152 K (phase III), 120 and

80 K (phase V) and 10 K (phase VII) on the NERA-PR neutron time-of-flight spectrometer of the IBR-2 pulsed reactor (FLNP JINR, Dubna) [18].
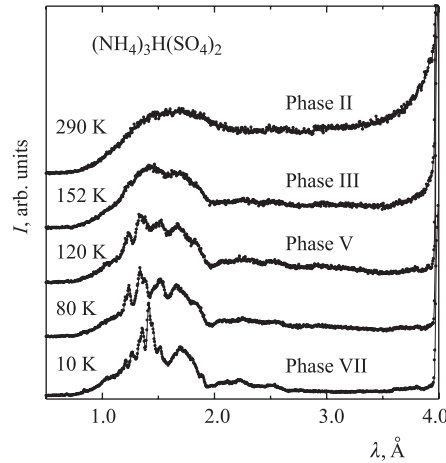

Fig. 5. The inelastic incoherent neutron scattering spectra for different phases of $(NH_4)_3H(SO_4)_2$

Thus, the availabilities of quasielastic incoherent neutron scattering at 290 K and six various positions on the toroid in nuclear density of $NH_4(2)$ point out that phase II of $(NH_4)_3H(SO_4)_2$ is really disordered due to the nuclear density of $NH_4(2)$ ammonium ions. Usually, the quasielastic incoherent neutron scattering can appear from molecular crystals, if molecules accomplish the reorientations around the crystal lattice axis of the symmetry or around the molecular axis of the symmetry. In accordance with differential Fourier maps of neutron densities of ammonium ions there is the possibility to suppose that $NH_4(2)$ ions are disordered.

The contribution of quasielastic incoherent neutron scattering to the inelastic incoherent neutron scattering spectrum at 152 K points out that phase III of $(NH_4)_3H(SO_4)_2$ can also have some disordered ammonium ions. It will be interesting to continue the complex X-ray and neutron single crystal diffraction study with the purpose of visualization of ammonium ion orientational positions in phase III of $(NH_4)_3H(SO_4)_2$ with the help of differential Fourier maps.

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