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NEUTRON SINGLE CRYSTAL DIFFRACTION
STUDIES OF ORIENTATIONAL GLASS STATE
IN THE $[\text{Rb}_x(\text{NH}_4)_{1-x}]_3\text{H}(\text{SO}_4)_2$ MIXED CRYSTALS

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Исследование состояния ориентационного стекла в смешанных кристаллах $[\text{Rb}_x(\text{NH}_4)_{1-x}]_3\text{H}(\text{SO}_4)_2$ методом нейтронной монокристаллической дифракции

Смешанные кристаллы $[\text{Rb}_x(\text{NH}_4)_{1-x}]_3\text{H}(\text{SO}_4)_2$ с концентрацией $x = 0,0$ обладают при комнатной температуре моноклинной структурой с пространственной группой $C2/c$, которая стабилизируется для $x > 0,09$ вплоть до низких температур. Ниже температуры «замерзания» $T_g = 30$ К эта система трансформируется в состояние ориентационного стекла.

Разностные карты Фурье для смешанных кристаллов $[\text{Rb}_x(\text{NH}_4)_{1-x}]_3\text{H}(\text{SO}_4)_2$ с $x = 0,0$ и $0,11$ при 293 К отражают разные ориентационные положения кристаллографически независимых групп $\text{NH}_4(1)$ и $\text{NH}_4(2)$. С другой стороны, разностные карты Фурье для $x = 0,20$ при 9 К в состоянии ориентационного стекла аналогичны для обеих аммониевых групп и отражают их статический ориентационный беспорядок.

Модулированная структура открыта в смешанных кристаллах $[\text{Rb}_x(\text{NH}_4)_{1-x}]_3\text{H}(\text{SO}_4)_2$ с $x = 0,11$ при 2 К, которая, однако, при этой температуре отсутствует для $x = 0,20$. Это наблюдение предполагает наличие на x - T фазовой диаграмме смешанных кристаллов $[\text{Rb}_x(\text{NH}_4)_{1-x}]_3\text{H}(\text{SO}_4)_2$ двух областей с разной структурой ориентационного стекла.

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Neutron Single Crystal Diffraction Studies of Orientational Glass State in the $[\text{Rb}_x(\text{NH}_4)_{1-x}]_3\text{H}(\text{SO}_4)_2$ Mixed Crystals

The $[\text{Rb}_x(\text{NH}_4)_{1-x}]_3\text{H}(\text{SO}_4)_2$ mixed crystal with the concentration $x = 0.0$ at room temperature crystallizes in a monoclinic $C2/c$ with sp. gr. (space group), which is stabilized for $x > 0.09$ down to low temperatures. This system is transformed in the orientational glass state below the freezing temperature $T_g = 30$ K.

The differential Fourier maps for the $[\text{Rb}_x(\text{NH}_4)_{1-x}]_3\text{H}(\text{SO}_4)_2$ mixed crystals show that if for $x = 0.0$ and 0.11 at 293 K the obtained maps reflect different orientational positions of crystallographically independent $\text{NH}_4(1)$ and $\text{NH}_4(2)$ groups, then the differential Fourier maps for $x = 0.20$ at 9 K in the orientational glass state are similar for both ammonium groups reflecting their static disorder.

The existence of the modulated structure in the $[\text{Rb}_x(\text{NH}_4)_{1-x}]_3\text{H}(\text{SO}_4)_2$ mixed crystals with $x = 0.11$ at 2 K is discovered, while the modulated structure for $x = 0.20$ at 2 K is absent. This observation supposes that there should be two different regions of the orientational glass state on x - T phase diagram of the $[\text{Rb}_x(\text{NH}_4)_{1-x}]_3\text{H}(\text{SO}_4)_2$ mixed crystals.

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

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INTRODUCTION

The $(\text{NH}_4)_3\text{H}(\text{SO}_4)_2$ (or TAHS) compound has high-temperature phase I with the property of superionic conductivity above 413 K [1] and below that temperature it undergoes the following sequence of phase transitions:

$$\text{I} \Rightarrow 413 \text{ K} \Rightarrow \text{II} \Rightarrow 265 \text{ K} \Rightarrow \text{III} \Rightarrow 139 \text{ K} \Rightarrow \text{IV} \Rightarrow 133 \text{ K} \Rightarrow \text{V} \Rightarrow 63 \text{ K} \Rightarrow \text{VII};$$

sp. gr. $R\bar{3}$	$C2/c$	sp. gr.	sp. gr. $P2/n$	sp. gr. $P2/n$	sp. gr. $P\bar{1}$	sp. gr.
[1]	[2-4]	[5]	[5]	[5]	?	?

All the above-mentioned publications about the determination of crystal structures for different phases of $(\text{NH}_4)_3\text{H}(\text{SO}_4)_2$ were fulfilled by means of the X-ray single crystal diffraction. It was shown that crystal structure of triammonium hydrogen disulfate consists of $(\text{SO}_4)\text{H}(\text{SO}_4)$ dimers and two types of crystallographically independent groups of ammonium ions, which are linked with sulfate ions by hydrogen bonds.

The phase transitions in TAHS are accompanied by the changes in orientational order of sulfate and ammonium ions and by ordering of hydrogen atoms in dimers. It is worth mentioning that hydrogen bond lengths for ammonium ions from the X-ray single crystal diffraction lie in the range from 0.78(3) to 1.02(5) Å in [2], from 0.70(3) to 0.81(4) Å in [3] and from 0.79(6) to 0.91(5) Å in [4]. Thus, the results of X-ray diffraction lead to the conclusion about deformed ammonium ions in TAHS.

It is shown by dielectric spectroscopy that the substitution of NH_4^+ ions for Rb^+ ions leads to complex x - T phase diagram of the $[\text{Rb}_x(\text{NH}_4)_{1-x}]_3\text{H}(\text{SO}_4)_2$ (or TRAHS) mixed crystals. Even small amount of rubidium significantly changes the sequence of phase transitions: 9 at.% of rubidium ions is enough to stabilize phase II down to low temperature. The dielectric spectroscopy study also shows the presence of the orientational glass state region below $T_g = 30$ K [6]. The x - T phase diagram of TRAHS is presented in Fig. 1.

It is known that the X-ray single crystal diffraction of the $[\text{Rb}_x(\text{NH}_4)_{1-x}]_3\text{H}(\text{SO}_4)_2$ mixed crystals with $x = 0.57$ was performed at room temperature and 180 K for the study of hydrogen bond character [7]. It was shown that the crystal structures of both doped and undoped reference crystals are the same and belong to monoclinic $C2/c$ sp. gr. This result confirms the conclusion of dielectric spectroscopy study of the stabilization of the phase II [6] in the $[\text{Rb}_x(\text{NH}_4)_{1-x}]_3\text{H}(\text{SO}_4)_2$ mixed crystals for $x > 0.09$. The two ammonium ions, whose atomic positions are determined for TRAHS in [7], occupy general position (8f) with the N-H distances from 0.873(3) to 0.984(2) Å and a special position (4e) with the N-H bond lengths from 0.804(1) to 0.858(1) Å.

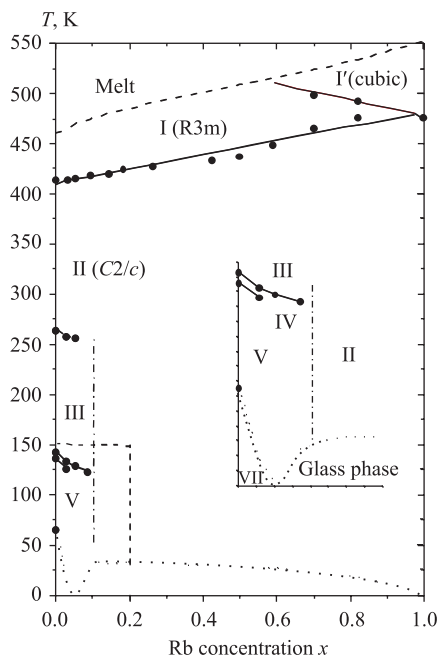


Fig. 1. The x - T phase diagram of the $[\text{Rb}_x(\text{NH}_4)_{1-x}]_3\text{H}(\text{SO}_4)_2$ mixed crystals

The purpose of the investigation is the refinement of crystal structures of phases II for TAHS and TRAHS with rubidium concentration $x = 0.11$ and 0.20 over a wide range of temperatures. The presented results contain the information about the neutron single crystal diffraction studies of the above-mentioned compounds on E5 and E2 diffractometers (BENSC, HMI, Berlin).

EXPERIMENTAL DATA AND RESULTS

The crystal structure refinement of the phases II of TAHS is carried out at room temperature, and corresponding diffraction studies of TRAHS with $x = 0.11$ and 0.20 are carried out in the range from room temperature to 2 K respectively.

The neutron single crystal diffraction studies are fulfilled on the E5 diffractometer and the experimental conditions of these measurements are presented in Table 1. The determined atomic positions for S, O, N1/Rb1 and N2/Rb2 for TAHS and TRAHS with $x = 0.11$ at room temperature and for TRAHS with $x = 0.20$ at $T = 9$ K are presented in Table 2. Table 2 contains only atomic positions of S, O and N/Rb. Hydrogen positions are not always exactly defined,

which has its consequence in insufficient R-factors. However, the obtained hydrogen positions in TAHS and TRAHS allow us to calculate N(1)-H_i and N(2)-H_i bond lengths (*i* = 1, 4).

Table 1. The experimental conditions, lattice parameters of [Rb_x(NH₄)_{1-x}]₃H(SO₄)₂ mixed crystals, C2/c sp. gr. Z = 4

Parameters	<i>x</i> = 0, <i>T</i> = 300 K	<i>x</i> = 0.11, <i>T</i> = 300 K	<i>x</i> = 0.20, <i>T</i> = 9 K
Wavelength	0.91400 Å	0.8902 Å	0.8900 Å
<i>a</i>	15.435(2) Å	15.261(3) Å	15.2730(15) Å
<i>b</i>	5.8647(12) Å	5.8027(12) Å	5.8156(6) Å
<i>c</i>	10.170(3) Å	10.065(2) Å	9.9326(10) Å
α	90°	90°	90°
β	101.83(3)°	101.81(3)°	102.667(0103)°
γ	90°	90°	90°
Crystal size	4×4×4 mm ³	4×4×3 mm ³	4×4×3 mm ³
Limiting indices	-24≤ <i>h</i> ≤23, -8≤ <i>k</i> ≤0, -9≤ <i>l</i> ≤15	-26≤ <i>h</i> ≤25, 0≤ <i>k</i> ≤9, 0≤ <i>l</i> ≤17	-3≤ <i>h</i> ≤25, -3≤ <i>k</i> ≤8, -10≤ <i>l</i> ≤16
Reflections collected / unique	1828 / 1596	2392/2010	998/909
Refinement method	Full-matrix least-squares on F ²	Full-matrix least-squares on F ²	Full-matrix least-squares on F ²
Data /restraints/ parameters	1596 / 0 / 102	1622 / 3 / 128	909/0/53
Goodness-of-fit on F ²	2.070	1.180	14.007
Final R indices R1/wR2	I>2sigma(I) 0.2019/0.5351	I>2sigma(I) 0.1206/0.2547	I>3sigma(I) 0.257/0.576

Table 2. The determined atomic positions for the [Rb_x(NH₄)_{1-x}]₃H(SO₄)₂ mixed crystals, C2/c sp. gr. Z = 4. Atomic coordinates are scaled as × 10⁴

Atoms	TAHS at <i>T</i> = 300 K			TRAHS (<i>x</i> = 0.11) at <i>T</i> = 300 K			TRAHS (<i>x</i> = 0.20) at <i>T</i> = 9 K		
	<i>x</i>	<i>y</i>	<i>z</i>	<i>x</i>	<i>y</i>	<i>z</i>	<i>x</i>	<i>y</i>	<i>z</i>
S	1163(6)	2524(13)	4482(9)	1142(4)	2177(9)	4627(6)	1150(13)	2521(13)	4580(20)
O1	156(4)	2509(14)	3933(13)	145(2)	1846(8)	4424(5)	189(7)	2300(20)	4270(20)
O2	1381(6)	2502(12)	3933(13)	1503(3)	2231(8)	6058(4)	1410(12)	2487(17)	6066(18)
O3	1471(5)	4564(11)	3944(8)	1289(3)	4328(7)	3981(5)	1428(5)	4634(17)	4010(9)
O4	1484(4)	481(11)	3938(7)	1490(3)	273(7)	3982(5)	1458(5)	336(15)	3991(9)
N1/Rb1	1993(2)	2510(5)	1469(3)	3012(2)	7757(4)	3471(2)	3015(4)	7530(6)	3550(7)
N2/Rb2	5000	2515(6)	2500	5000	2305(5)	2500	5000	2511(7)	2500

The average N-H bond length over different ammonium ions of TAHS and TRAHs is 0.98 Å and this value is larger than the N-H bond lengths obtained by X-ray single crystal diffraction and with less dispersion [2–4]. Thus, ammonium ions from neutron single crystal diffraction data can be presented by regular tetrahedra.

The anisotropic thermal parameters are presented by thermal ellipsoids for ammonium ions NH₄(1) and NH₄(2), for H and sulfate ions forming dimers in Fig. 2.

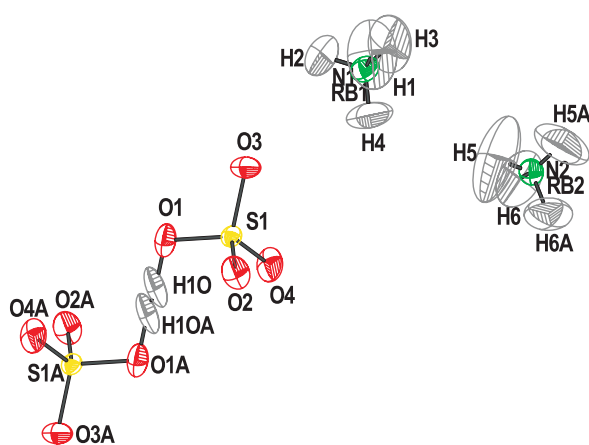


Fig. 2. The anisotropic thermal parameters of the $[\text{Rb}_x(\text{NH}_4)_{1-x}]_3\text{H}(\text{SO}_4)_2$ mixed crystals with ammonium ions NH₄(1) and NH₄(2) and (SO₄)H(SO₄), dimer $C2/c$ sp. gr., $Z = 4$, at room temperature

The crystal packing of the $[\text{Rb}_x(\text{NH}_4)_{1-x}]_3\text{H}(\text{SO}_4)_2$ mixed crystal with $x = 0.11$ at room temperature is presented in Figs. 3 and 4 for different projections.

A comparison of the Fo–Fc differential nuclear density maps (contours from 0.0 every 0.5 1/Å³) for the $[\text{Rb}_x(\text{NH}_4)_{1-x}]_3\text{H}(\text{SO}_4)_2$ mixed crystals with $x = 0.0$ at 300 K, with $x = 0.11$ at 300 K and with $x = 0.20$ at 9 K for NH₄(1)/Rb(1) and (NH₄(2)/Rb(2) groups are presented in Figs. 5 and 6 respectively.

For the comparison of the Fo–Fc differential nuclear density maps, the cross sections inside a unit cell are presented on 0.45 Å above the XZ plane passing through N(1)/N(2) atom, in the XZ plane passing through N(1)/N(2) atom and on 0.45 Å below the above-mentioned XZ plane.

The presented Fo–Fc differential nuclear density maps for NH₄(1)/Rb(1) and NH₄(2)/Rb(2) groups show that orientations of these groups are different for $[\text{Rb}_x(\text{NH}_4)_{1-x}]_3\text{H}(\text{SO}_4)_2$ on different cross sections for crystals with $x = 0.0$

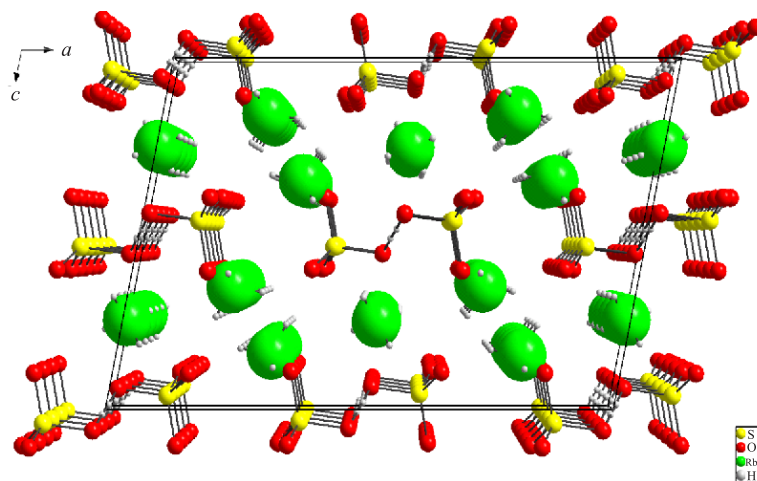


Fig. 3. The projection of $[\text{Rb}_x(\text{NH}_4)_{1-x}]_3\text{H}(\text{SO}_4)_2$ ($x = 0.11$ at room temperature) along the Y -axis $[010]$

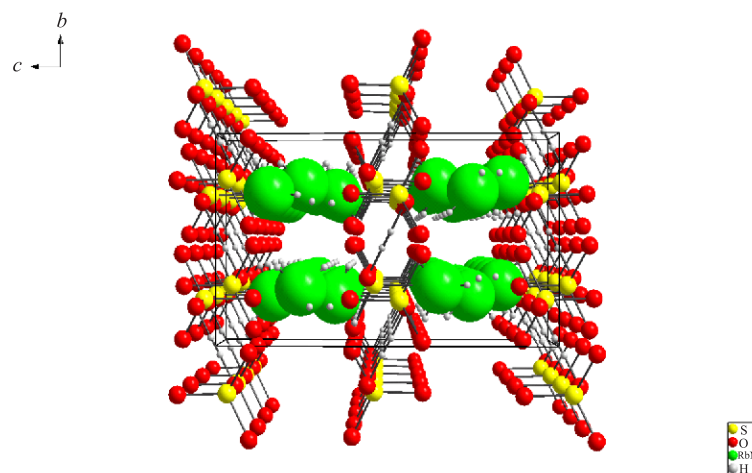


Fig. 4. The projection of $[\text{Rb}_x(\text{NH}_4)_{1-x}]_3\text{H}(\text{SO}_4)_2$ ($x = 0.11$ at room temperature) along the X -axis $[100]$

and $x = 0.11$ at $T = 300$ K. This indicates that different orientations of ammonium groups are present as a function of rubidium concentration even in phase II. However, similar Fo–Fc differential nuclear density maps for $\text{NH}_4(1)/\text{Rb}(1)$ and $\text{NH}_4(2)/\text{Rb}(2)$ groups of crystals with $x = 0.20$ at 9 K, which correspond to orientational glass state, show a certain analogy between Fo–Fc differential nu-

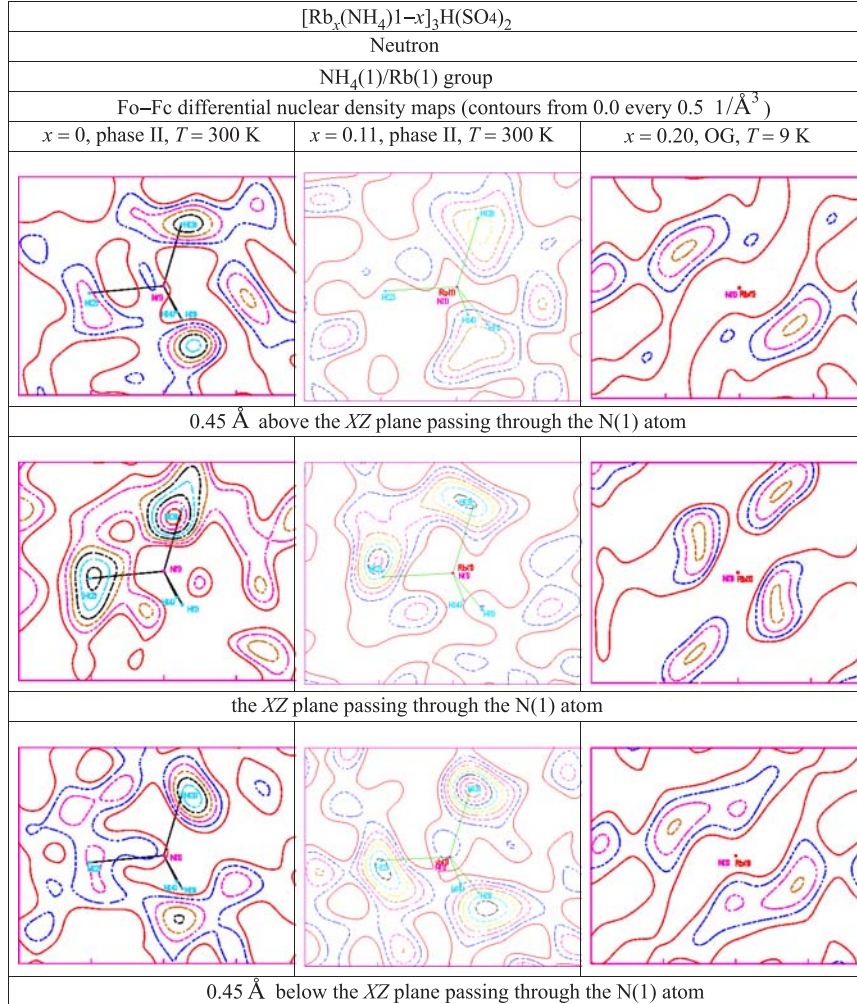


Fig. 5. The Fo-Fc differential nuclear density maps (contours from 0.0 every 0.5 1/Å³) near N(1)/Rb(1) atom of the [Rb_x(NH₄)_{1-x}]₃H(SO₄)₂ mixed crystals

clear density maps for these groups. If in orientational glass state NH₄(1)/Rb(1) and NH₄(2)/Rb(2) groups inside the unit cell are oriented stochastically, then the intensities of Bragg reflections contain the contribution of all possible orientations over the whole crystal. This situation can suggest the formation of the average orientational distribution over these NH₄(1)/Rb(1) and NH₄(2)/Rb(2) ammonium groups in orientational glass state.

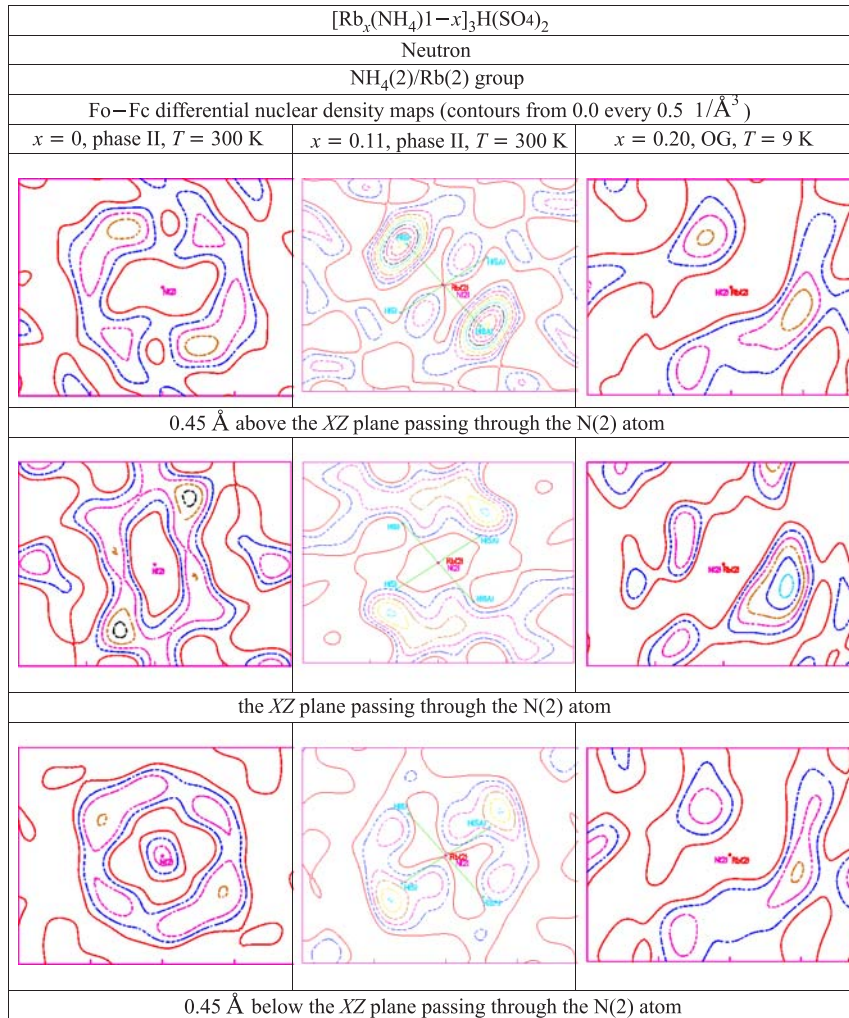


Fig. 6. The Fo–Fc differential nuclear density maps (contours from 0.0 every 0.5 1/Å³) near N(2)/Rb(2) atom for the [Rb_x(NH₄)_{1-x}]₃H(SO₄)₂ mixed crystals

U.Höchli, K. Knorr, and A. Loidl have foreseen that the crystal structure of the orientational glass may be modulated. They wrote in their review «Orientational glass» [8] about the formation of modulated structure: «Modulated patterns

of displacements, titles or orientations lead to satellite peaks at the positions

$$\mathbf{q} = \boldsymbol{\tau}_{hkl} \pm \mathbf{q}_0, \quad (1)$$

where \mathbf{q}_0 is the propagation vector of the modulation». Here $\boldsymbol{\tau}_{hkl}$ present vectors in reciprocal lattice with Miller indices (hkl) .

The idea of U.Höchli, K.Knorr, and A.Loidl stimulated the diffraction studies of changes in crystal structures of substances in the process of phase transition into orientational glass state below the «freezing» temperature T_g . It was discovered that the transition into orientation glass state is observed on the x - T phase diagram of the $K_{1-x}(\text{NH}_4)_x\text{I}$ mixed crystal in the middle-concentration region [9]. Soon it was shown that in these mixed crystals the increase in correlation length as a function of concentration [10] and the diffuse scattering [11] are observed below T_g .

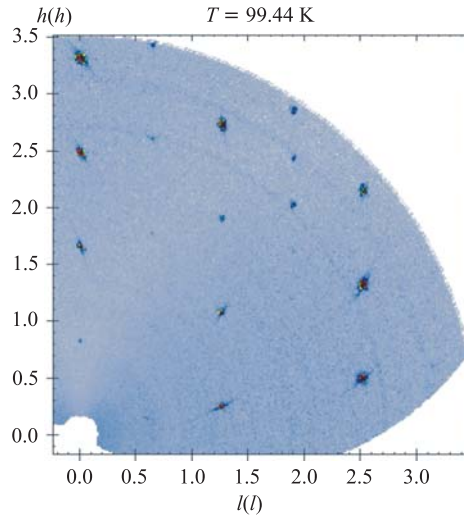


Fig. 7. The diffraction patterns from the $(\text{Rb}_{0.11}(\text{NH}_4)_{0.89})_3\text{H}(\text{SO}_4)_2$ mixed crystal in (X^*Z^*) plane at 100 K

Indeed such a situation arises during the study of crystal structure of the $[\text{Rb}_x(\text{NH}_4)_{1-x}]_3\text{H}(\text{SO}_4)_2$ mixed crystals. The measurements of neutron diffraction patterns from sample of single crystal TRAHS with $x = 0.11$ in two different orientations on E2 diffractometer for the first time led to the observation of the satellite reflections near some Bragg reflections. Diffraction patterns from sample with $x = 0.11$ at $T = 100$ K are presented in Fig. 7 and at temperature $T = 2$ K, in Fig. 8.

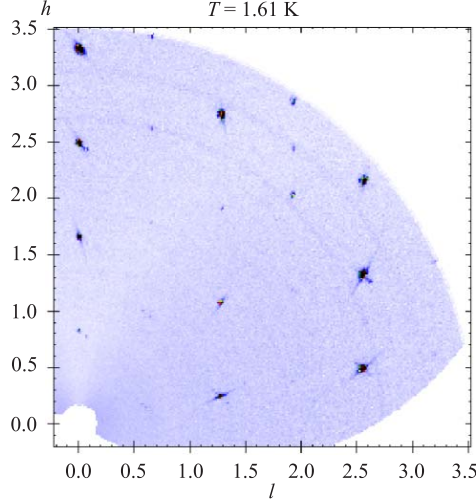


Fig. 8. The diffraction patterns from the $(\text{Rb}_{0.11}(\text{NH}_4)_{0.89})_3\text{H}(\text{SO}_4)_2$ mixed crystal in (X^*Z^*) plane at 2 K

A comparison of the presented diffraction patterns for sample with $x = 0.11$ in (X^*Z^*) plane at $T = 100$ and 2 K shows the appearance of additional peaks of weak intensities near some Bragg reflections at $T = 2$ K. Bragg reflections with Miller indices (200), (400), (600), (002), (004), and (204) at $T = 100$ K and these Bragg reflections at $T = 2$ K with weak intensities of satellite peaks are presented separately in Fig. 9. Figure 10 simulates the diffraction patterns from the $(\text{Rb}_{0.11}(\text{NH}_4)_{0.89})_3\text{H}(\text{SO}_4)_2$ mixed crystal at $T = 2$ K in (X^*Z^*) plane. It is possible to draw lines which will go through the Bragg reflections (800) and (204), (600) and (004), (400) and (-204), (300) and (002), and (200) and (-404). One can get a sight of satellite reflections near Bragg reflections (204), (600), (004), (400), (002), and (200) placed on these lines, which are parallel to vector

$$\mathbf{Q} = -1.5\mathbf{a}^* + \mathbf{c}^*. \quad (2)$$

Such a coincidence of positions of satellite reflections with single orientation gives support to the observation of modulated structure in the $(\text{Rb}_{0.11}(\text{NH}_4)_{0.89})_3\text{H}(\text{SO}_4)_2$ mixed crystal in orientational glass state.

The corresponding measurements with the $[\text{Rb}_{0.20}(\text{NH}_4)_{0.80}]_3\text{H}(\text{SO}_4)_2$ mixed crystal at $T = 100$ and 2 K in (X^*Z^*) plane do not detect satellite reflections. Thus, experimental data show the existence of two different region of orientational glass state on x - T phase diagram of the $[\text{Rb}_x(\text{NH}_4)_{1-x}]_3\text{H}(\text{SO}_4)_2$ mixed crystals.

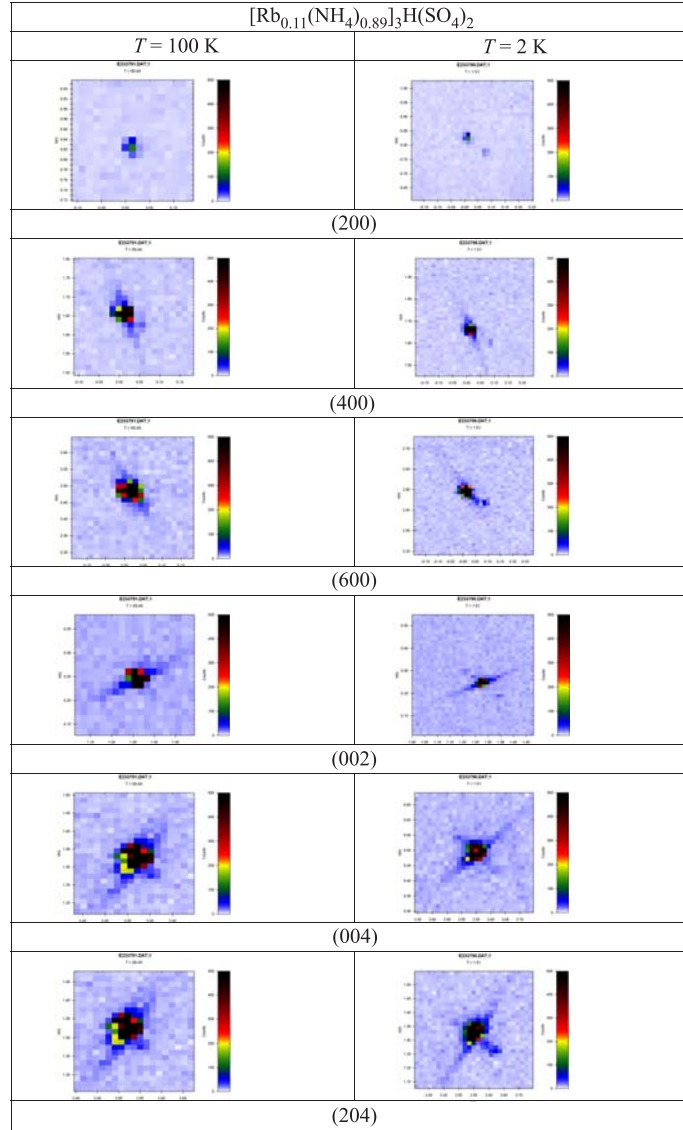


Fig. 9. The appearance of weak satellite reflections at 2 K near corresponding Bragg reflections in the (X^*Z^*) plane

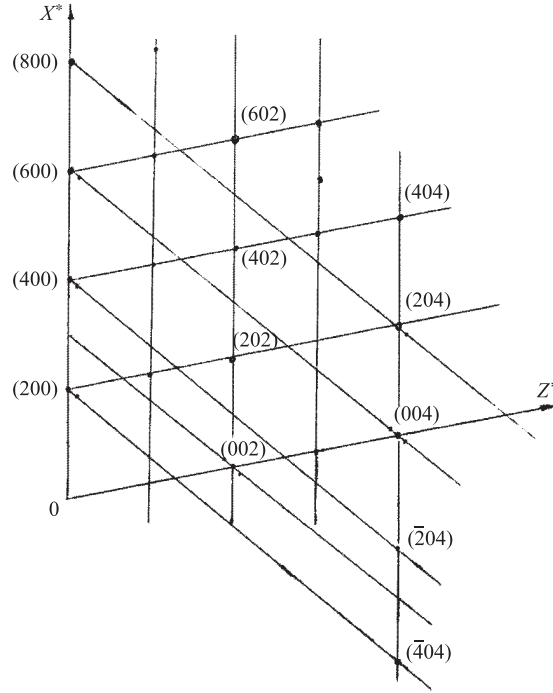


Fig. 10. The presentation of the reciprocal lattice with the direction of the modulation vector in the (X^*Z^*) plane. The modulation vector is parallel to vector $\mathbf{Q} = -1.5\mathbf{a}^* + \mathbf{c}^*$

CONCLUSIONS

The results of single crystal neutron diffraction investigations of the $(\text{Rb}_x(\text{NH}_4)_{1-x})_3\text{H}(\text{SO}_4)_2$ mixed crystals allow us to draw the following conclusions:

— the ammonium ion can be treated as regular tetrahedron and, thus, the refinement of crystal structure of the $[\text{Rb}_x(\text{NH}_4)_{1-x}]_3\text{H}(\text{SO}_4)_2$ mixed crystals can be treated on the basis of the theory of W. Press and A. Hüller [12];

— differential Fourier maps for ammonium crystallographically independent groups $\text{NH}_4(1)$ and $\text{NH}_4(2)$ of the $[\text{Rb}_{0.20}(\text{NH}_4)_{0.80}]_3\text{H}(\text{SO}_4)_2$ mixed crystals at 9 K in the region of orientational glass state show that they can be treated as similar and reflect average orientations of ammonium groups. The visual demonstration of crystal structure in orientation glass state with the help of differential Fourier maps is materialized for the first time;

— a modulated structure of orientation glass formed in the $[\text{Rb}_x(\text{NH}_4)_{1-x}]_3\text{H}(\text{SO}_4)_2$ mixed crystal is observed;

— it is shown that in the $[\text{Rb}_x(\text{NH}_4)_{1-x}]_3\text{H}(\text{SO}_4)_2$ mixed crystal with $x = 0.11$ modulated patterns are observed at $T = 2$ K, and for mixed crystal with $x = 0.20$ at $T = 2$ K satellite peaks are not observed;

— the region of orientational glass state at x - T phase diagram of the $[\text{Rb}_x(\text{NH}_4)_{1-x}]_3\text{H}(\text{SO}_4)_2$ mixed crystals is presented by two concentration regions OG1 and OG2 with the boundary between $x = 0.11$ and $x = 0.20$. In this case OG1 region has modulated crystal structure and OG2 region is not modulated.

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