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REFINEMENT OF HYDROGEN POSITIONS IN $(NH_4)_2SeO_4$

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Лоозе А. и др. E14-2005-1
Уточнение водородных позиций в $(NH_4)_2SeO_4$

Изучение кристаллической структуры селената аммония проведено с помощью монокристальной рентгеновской и нейтронной дифракции с целью уточнения водородных позиций. Уточненные водородные позиции, полученные с помощью монокристальной нейтронной дифракции, показывают, что N–H длины связей соответствуют иону аммония как действительно регулярному тетраэдру. Монокристальная рентгеновская дифракция показывает, что N–H длины связей короче по сравнению с полученными с помощью нейтронной дифракции и не равны между собой. Таким образом, сравнение результатов рентгеновской и нейтронной дифракций дает основание предположить, что более короткие N–H длины связей, полученные с помощью рентгеновской дифракции, отражают распределение зарядов электронной плотности ионов аммония внутри кристаллической решетки $(NH_4)_2SeO_4$.

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Loose A. et al. E14-2005-1
Refinement of Hydrogen Positions in $(NH_4)_2SeO_4$

The crystal structure of ammonium selenate has been studied by means of single crystal X-ray and neutron diffraction with the purpose of the refinement of hydrogen positions. The refined hydrogen positions obtained by single crystal neutron diffraction show that N–H bond lengths form a regular tetrahedron in an ammonium ion. The single crystal X-ray diffraction data show that N–H bond lengths are shorter than those obtained by neutron diffraction and are not equal between themselves. Thus, the comparison of the results of X-ray and neutron diffraction allows one to suggest that the shorter N–H bond lengths obtained by X-ray diffraction reflect the distribution of the electron charge density of ammonium ions within the $(NH_4)_2SeO_4$ crystal lattice.

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

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INTRODUCTION

Until recently ammonium selenate, $(NH_4)_2SeO_4$, or ASE, has been known as a compound which has a monoclinic crystal structure at room temperature as determined by X-ray diffraction in [1]. Not long ago a communication appeared saying that a phase transition above room temperature, i. e., from 380 to 400 K, possibly via an intermediate phase was observed in it [2]. The high temperature crystal structure of ASE was not determined in this communication. On the other hand, the authors indicated that they did not observe any phase transition from 300 to 5 K.

The crystal structure of ammonium selenate as determined in the X-ray investigation [1] has a monoclinic unit cell with sp. gr. C2/m, Z = 4 and lattice parameters a = 12.152(6) Å, b = 6.418(3) Å and c = 7.711(4) Å, β = 115.50(12)° at room temperature. The results of the X-ray study [1] show that the ammonium groups are deformed and the N–H bond lengths differ significantly from those in a free NH_4^+ ion.

The objective of the recent investigation is the refinement of hydrogen positions in ASE with the help of X-ray and neutron single crystal diffraction.

EXPERIMENTAL RESULTS AND DISCUSSION

The investigated ASE single crystal was prepared using the reaction of synthesis in an aqueous medium:

$$CuSeO_4 + (NH_4)_2S \rightarrow CuS + (NH_4)_2SeO_4.$$

The refinement of the crystal structure of $(NH_4)_2SeO_4$ was carried out by single crystal X-ray and neutron diffraction. The X-ray diffraction and neutron diffraction measurements were performed at room temperature on the Kuma4CCD X-ray diffractometer (Warsaw University, Chemistry Department, Poland) and the E5 neutron four-circle diffractometer (BENSC HMI, Berlin, Germany), respectively. The conditions of the measurements, including experimental temperatures, used wavelengths, refined space group, obtained lattice parameters, number of measured reflections, number of unique reflections used for refining of atomic positions and the refinement results, are presented in Table 1.

The experimental X-ray and neutron data were processed using the programs [3, 4]. The atomic positions in $(NH_4)_2SeO_4$ and U_{eq} equivalent isotropic displacement parameters at 290 K refined by means of X-ray diffraction are presented in

Table 1. The conditions of measurements

Formula	$(NH_4)_2SeO_4$	
	X-ray	Neutron
Temperature	290 K	290 K
Wavelength	0.71073 Å	0.9019 Å
Space group	C2/m	C2/m
a	12.127(2) Å	12.4319(43) Å
b	6.4200(9) Å	6.5744(36) Å
c	7.700(1) Å	7.8845(31) Å
β	115.44(2)^o	115.51(2)°
Number of reflections	4911	1055
Unique reflections	721	874
$R1$	0.074	0.0677

Table 2a. The U_{eq} were defined as one third of the trace of the orthogonalized U_{ij} tensor.

Table 2a. The atomic positions in $(NH_4)_2SeO_4$ (from X-ray diffraction refinement)

Atom	x	y	z	Occup.	U_{eq} [Å^2]
Se	0.175(1)	0.0	0.218(1)	0.5	0.018(1)
O(1)	0.322(2)	0.0	0.361(4)	0.5	0.033(1)
O(2)	0.097(3)	0.0	0.344(4)	0.5	0.034(1)
O(3)	0.144(2)	0.209(3)	0.086(5)	1.0	0.030(1)
N(1)	0.517(3)	0.0	0.246(5)	0.5	0.028(1)
N(2)	0.842(3)	0.0	0.261(5)	0.5	0.023(1)
H(1)	0.458(5)	0.0	0.288(7)	0.5	0.03(1)
H(2)	0.907(7)	0.0	0.266(9)	0.5	0.06(2)
H(3)	0.568(5)	0.0	0.366(8)	0.5	0.03(1)
H(4)	0.855(5)	0.0	0.372(8)	0.5	0.03(1)
H(5)	0.525(3)	–0.106(5)	0.189(5)	1.0	0.034(9)
H(6)	0.800(4)	–0.103(6)	0.200(5)	1.0	0.030(8)

The atomic positions in $(NH_4)_2SeO_4$ and U_{eq} equivalent isotropic displacement parameters at 290 K refined by means of neutron diffraction are presented in Table 2b. The U_{eq} is defined as one third of the trace of the orthogonalized U_{ij} tensor.

The anisotropic displacement parameters obtained by means of neutron diffraction at 290 K for $(NH_4)_2SeO_4$ are presented in Table 3.

The anisotropic displacement factor exponent takes the form: $-2\pi^2[H^2a^{*2}U_{11} + \ldots + 2HKa^*b^*U_{12}]$.

Table 2b. The atomic positions in $(NH_4)_2SeO_4$ (from neutron diffraction refinement)

Atom	x	y	z	Occup.	U_{eq} [Å^2]
Se	0.175 (2)	0.0	0.218(3)	0.5	0.0202(4)
O(1)	0.322(3)	0.0	0.360 (5)	0.5	0.0360(8)
O(2)	0.096 (3)	0.0	0.344(5)	0.5	0.0367(9)
O(3)	0.144(2)	0.209 (4)	0.086(3)	1.0	0.0323(5)
N(1)	0.517(2)	0.0	0.245 (3)	0.5	0.0317(5)
N(2)	0.842(2)	0.0	0.261 (3)	0.5	0.0274(4)
H(1)	0.437(7)	0.0	0.262(1)	0.5	0.057(2)
H(2)	0.923 (8)	0.0	0.253(1)	0.5	0.056(2)
H(3)	0.585(7)	0.0	0.384(1)	0.5	0.061
H(4)	0.856 (6)	0.0	0.402 (9)	0.5	0.046
H(5)	0.527(9)	0.126(1)	0.176(9)	1.0	0.072
H(6)	0.791(6)	0.126(1)	0.195(8)	1.0	0.057

Table 3. The thermal parameters for atoms in $(NH_4)_2SeO_4$ (neutron diffraction refinement results). The anisotropic displacement factor exponent takes the form: $-2\pi^2$[$H^2a{*}^2U_{11}$ +...+2HK$a^*b^*U_{12}$] and U_{ij} are presented in Å^2

Atom	U11	U22	U33	U23	U13	U12
Se	0.0179(7)	0.0255(1)	0.0178(7)	0.0	0.0084(6)	0.0
O(1)	0.0208(1)	0.0544(2)	0.0279(1)	0.0	0.0060(1)	0.0
O(2)	0.0295(1)	0.0607(3)	0.0243(1)	0.0	0.0158(1)	0.0
O(3)	0.0368(1)	0.0266(11)	0.0315(9)	0.0058(8)	0.0129(8)	–0.0002(9)
N(1)	0.0377(9)	0.0292(1)	0.0295(8)	0.0	0.0159(7)	0.0
N(2)	0.0303(9)	0.0286(1)	0.0235(7)	0.0	0.0118(7)	0.0
H(1)	0.0428(3)	0.0734(6)	0.0557(4)	0.0	0.0210(3)	0.0
H(2)	0.0566(4)	0.0696(6)	0.0569(4)	0.0	0.0378(4)	0.0
H(3)	0.0436(3)	0.0963(8)	0.0460(4)	0.0	0.0207(3)	0.0
H(4)	0.0465(3)	0.0613(5)	0.0349(3)	0.0	0.0212(2)	0.0
H(5)	0.1169(6)	0.0515(4)	0.0583(3)	0.0098(3)	0.0485(4)	–0.0041(4)
H(6)	0.0677(33)	0.0473(3)	0.0520(3)	0.0104(2)	0.0211(2)	0.0158(3)

The S–O(I) and N(1)–H(J) and N(2)–H(J) bond lengths in $(NH_4)_2SeO_4$ determined with the help of recent X-ray and neutron diffraction measurements are presented in Table 4. A compasion of average S–O(I), N(1)–H(J) and N(2)–H(J) bond lenghts shows that the bond lengths determined by X-ray diffraction are shorter than those determined by neutron diffraction.

The comparison points to that there takes place a change in the electronic charge density if a chemical bond between SeO_4^{-2} and NH_4^+ ions in the crystal lattice is formed. The S-O(I) average bond lengths determined by X-ray diffraction in [1] are longer than those obtained in a recent X-ray study by 0.012 Å and

Table 4. The bond lengths for $NH_4(1)$, $NH_4(2)$ and SeO_4 ions

Atoms	X-ray, Å (from [1])	Neutron, Å	X-ray, Å	Calculation, Å
Se–O(1)	1.645(8)	1.682(4)	1.638(2)	
Se–O(2)	1.644(8)	1.667(4)	1.628(3)	
Se–O(3)	1.643(5)	1.667(3)	1.630(2)	
mean	**1.644(7)**	**1.672(4)**	**1.632(2)**	
SeO_4^{-2} Se-O				**1.654**
N(1)–H(1)	0.890	1.057(4)	0.91(6)	
N(1)–H(3)	0.936	1.052(4)	0.86(6)	
N(1)–H(5)	0.861	1.029(8)	0.84(4)	
mean	**0.896**	**1.046(5)**	**0.87(5)**	
N(2)–H(2)	0.947	1.045(6)	0.78(8)	
N(2)–H(4)	0.922	1.047(8)	0.80(6)	
N(2)–H(6)	0.94	1.035(7)	0.85(4)	
mean	**0.936**	**1.042(7)**	**0.81(6)**	
NH_4^+ N-H				**1.012**

are shorter than those obtained in the neutron diffraction study by 0.028 Å. The comparison of the averages of the N(1)–H(J) and N(2)–H(J) bond lengths with those obtained in [1] cannot be correct as the determination of hydrogen positions in [1] is just approximate. The authors [1] determined the hydrogen positions from the difference map and they were not involved in a full–matrix least squares refinement. The final refinement was carried out with fixed H positions obtained from the difference map.

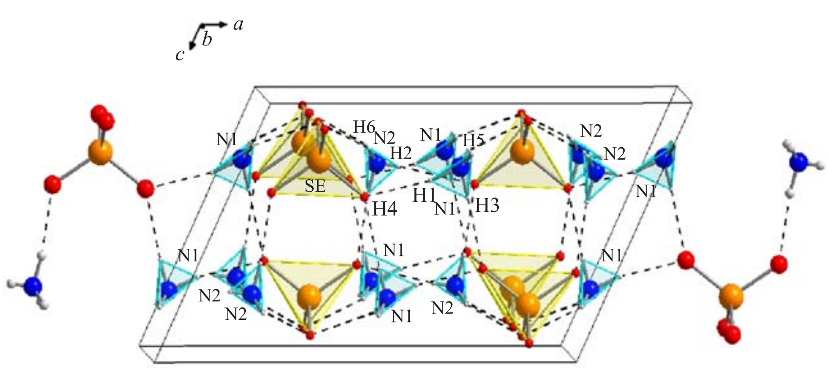


Fig. 1. The $(NH_4)_2SeO_4$ unit cell as a projection on the (ac) plane

A comparison of the N(2)–H(J) average bond length from [1] with that from a recent X-ray study shows that they differ by 0.126 Å. It is interesting to compare the obtained average S–O(I) and N-H(I) bond lengths with those calculated for free SeO_4^{-2} and NH_4^+ ions. The calculation of the configuration for free SeO_4^{-2} and NH_4^+ ions was carried out with the GAUSSIAN98 program [5]. On the basis of the Hartree–Fock method and 6–31G* electron wave functions there was

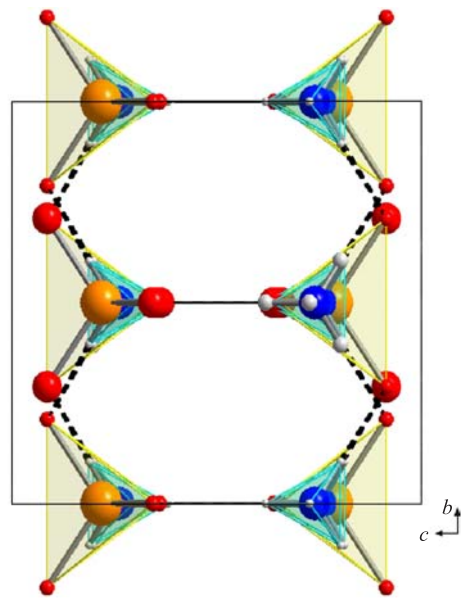


Fig. 2. The $(NH_4)_2SeO_4$ unit cell as a projection on the (bc) plane

accepted the HF/6-31G* model. The calculated S–O and N–H bond lengths are presented in Table 4. The S–O and N–H bond lengths obtained from the neutron diffraction experiment are longer than those calculated for free ions by 0.018 and 0.032 Å, respectively.

However, analysis of recent single crystal X-ray and neutron diffraction studies shows an insignificant spread in the values of bond lengths for S-O(I), N(1)-H(I) and N(2)-H(J) prompting the conclusion that in a $(NH_4)_2SeO_4$ ammonium selenate ion each ammonium ion can be considered as a nearly regular tetrahedron.

A $(NH_4)_2SeO_4$ unit cell is presented in Fig. 1 as a projection on the (ac) plane, in Fig. 2 as a projection on the (bc) plane and in Fig. 3 as a projection on the (ab) plane.

It is interesting to carry out a comparison between differential Fourier electronic charge density and differential Fourier nuclear density maps obtained by

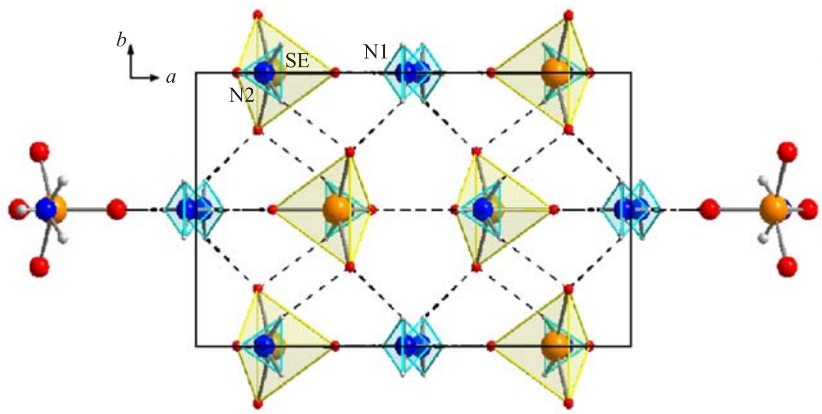


Fig. 3. The $(NH_4)_2SeO_4$ unit cell as a projection on the (ab) plane

X-ray and neutron diffraction, respectively. The corresponding Fourier maps for $NH_4(1)$ and $NH_4(2)$ groups are presented in Figs. 4 and 5, respectively.

The differential Fourier nuclear density map for the $NH_4(1)$ ion is the cross section in the XZ plane going through the N(1) atom showing two hydrogen atoms of the ammonium tetrahedron edge lying in the XZ mirror plane. The cross sections above the XZ plane going through N(1) at a step of 0.45 and 0.85 Å show an increase in the hydrogen density related with a top hydrogen atom in the tetrahedron. There is another top hydrogen atom lying symmetrically below the XZ plane going through the N(1) atom due to the mirror plane.

The differential Fourier electron charge density maps at 0.45 and 0.85 Å above the XZ plane going through the N(I) atom are similar to differential Fourier nuclear density maps. However, the differential Fourier electron charge density map and the nuclear density map in the XZ plane going through the N(I) atom are different.

The differential Fourier electron charge density and nuclear density maps for the N(2) ion are similar to analogous maps for the N(1) ion except for two hydrogen atoms form the ammonium tetrahedron edge which has a somewhat different orientation in the XZ mirror plane. The differential Fourier electron charge density maps at 0.45 and 0.85 Å above the XZ plane through the N(2) atom are similar to differential Fourier nuclear density maps.

CONCLUSION

The obtained single crystal X-ray and neutron diffraction results show that the N–H bond lengths of ammonium ions in $(NH_4)_2SeO_4$ determined with the help of X-ray diffraction differ from those determined by neutron diffraction.

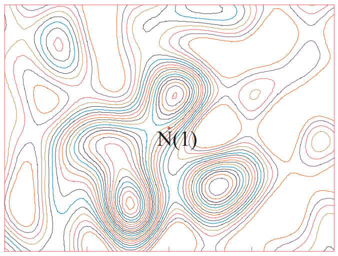
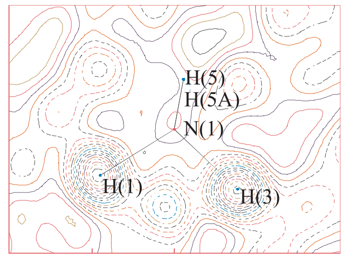
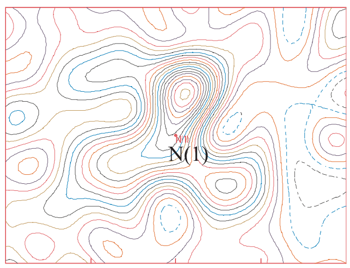
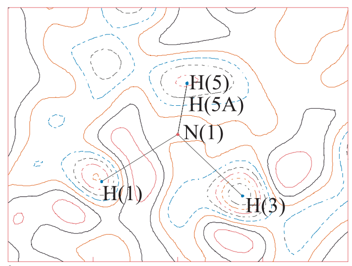
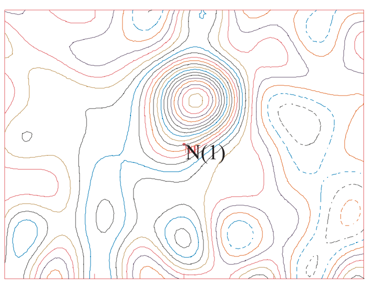
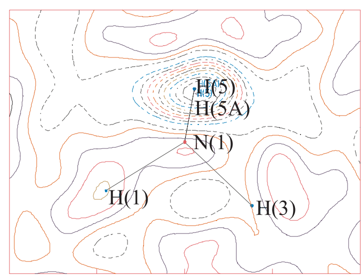
X-ray Fo–Fc differential electron density map (contours every 0.05 1/Å^3)	Neutron Fo–Fc differential electron density map (contours every 0.5 1/Å^3)
 the *XZ* plane passed through N(1) atom	 the *XZ* plane passed through N(1) atom
 0.45 Å above the *XZ* plane passed through N(1) atom	 0.45 Å above the *XZ* plane passed through N(1) atom
 0.85 Å above the *XZ* plane passed through N(1) atom	 0.85 Å above the *XZ* plane passed through N(1) atom

Fig. 4. The differential Fourier electron charge density and nuclear density maps for the $NH_4(1)$ group obtained by *X*-ray and neutron diffraction, respectively

The average values of the N–H bond lengths of ammonium ions in $(NH_4)_2SeO_4$ determined by single crystal *X*-ray and neutron diffraction are 0.84 and 1.044 Å,

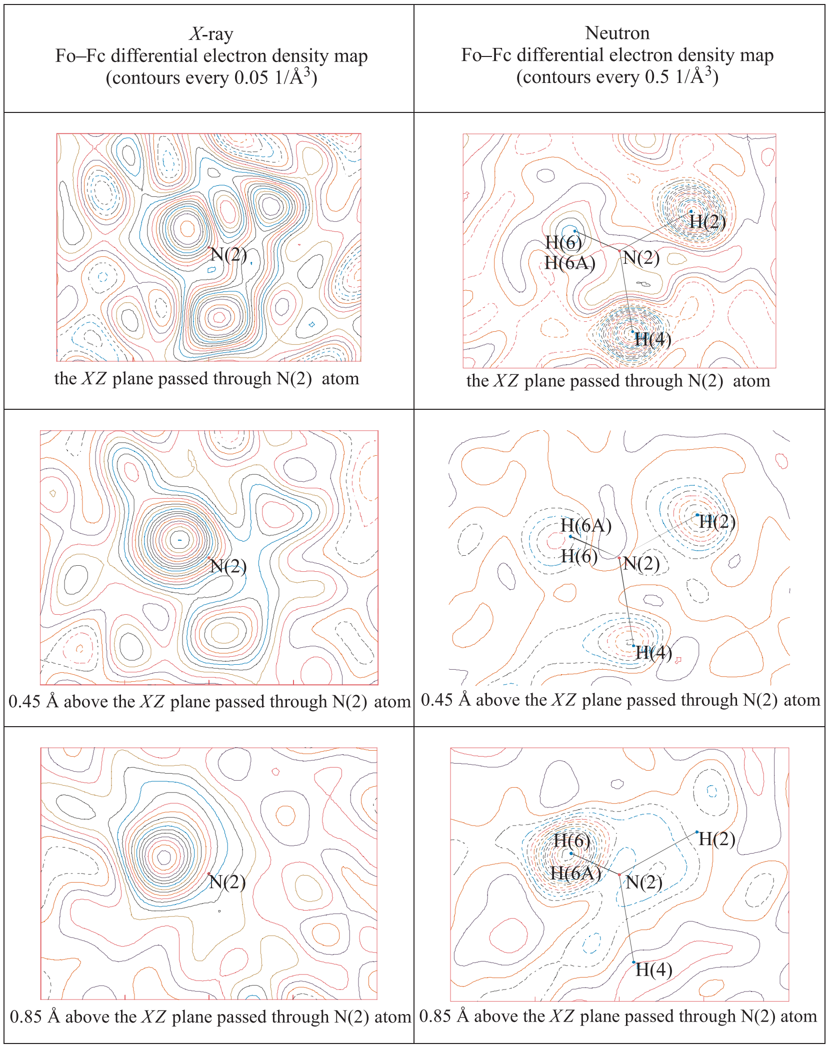


Fig. 5. The differential Fourier electron charge density and nuclear density maps for the $NH_4(2)$ group obtained by X-ray and neutron diffraction, respectively

respectively. However, the configurations of SeO_4^{-2} and NH_4^+ ions can be considered as a nearly regular tetrahedron. On the other hand, the electronic charge density and nuclear density maps for the $NH_4(1)$ and $NH_4(2)$ groups are similar showing the localization of ammonium ions in the monoclinic phase of $(NH_4)_2SeO_4$.

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