E14-2005-133

A. Loose[1], L. S. Smirnov[2,3], V. V. Dolbinina[4],
L. M. Yakovleva[4], V. V. Grebenev[4]

THE REFINEMENT OF HYDROGEN POSITIONS IN PHASE II OF β-$LiNH_4SO_4$

Submitted to «Zeitschrift für Kristallographie»

[1] BENSC, Hahn-Meitner Institute, Berlin, Germany
[2] FSUE SSC FR Institute of Theoretical and Experimental Physics, Moscow
[3] Frank Laboratory of Neutron Physics JINR, Dubna
[4] A. V. Shubnikov Institute of Crystallography of RAS, Moscow

Лоозе А. и др. E14-2005-133

Уточнение положений атомов водорода в фазе II β-$LiNH_4SO_4$

Определение положений атомов и тепловых параметров кристаллической структуры β-$LiNH_4SO_4$ в фазе II проведено с помощью монокристаллической нейтронной дифракции при комнатной температуре с целью уточнения длин связей N–H ионов аммония. Набор данных интенсивностей отражений Брегга выполнен на дифрактометре E5, установленном в BENSC (HMI, Берлин, Германия). В результате положения атомов и тепловые параметры определены с помощью метода наименьших квадратов с R = 0,072 и wR = 0,057. Показано, что ионы аммония могут быть представлены регулярными тетраэдрами.

Работа выполнена в Лаборатории нейтронной физики им. И. М. Франка ОИЯИ.

Препринт Объединенного института ядерных исследований. Дубна, 2005

Loose A. et al. E14-2005-133

The Refinement of Hydrogen Positions in Phase II of β-$LiNH_4SO_4$

The determination of the atomic positions and thermal parameters of the crystal structure for phase II of β-$LiNH_4SO_4$ is carried out by the single crystal neutron diffraction at room temperature for the purpose to refine N–H bond lengths for ammonium ions. The acquisition of intensities from Bragg reflections is fulfilled on the E5 diffractometer set in BENSC (HMI, Berlin, Germany). Atomic positions and thermal parameters are determined by the least-square method with R = 0.072 and wR = 0.057. It is shown that ammonium ions can be presented as regular tetrahedra.

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

Preprint of the Joint Institute for Nuclear Research. Dubna, 2005

INTRODUCTION

The β-$LiNH_4SO_4$ (LAS) undergoes the series of phase transitions: phase I $\Leftrightarrow$ 459.6 K [1] $\Leftrightarrow$ phase II $\Leftrightarrow$ 284 K [2] $\Leftrightarrow$ phase III $\Leftrightarrow$ 27 K [3] $\Leftrightarrow$ phase IV. Phase I (Pmcn-D_{2h}^{16}, Z = 4 [4]) displays paraelectricity, phase II ($P2_1$cn-C_{2v}^{9}, Z = 4 [5, 6]) is ferroelectric, phase III ($P2_1/c$-C_{2h}^{5}, Z = 8 [6]) is ferroelastic and phase IV has the symmetry Cc-C_s^4[3].

The crystal structures of all phases of LAS were determined earlier only with the help of x-ray single crystal diffraction. The hydrogen positions in phases II and III were determined in [5, 6]. The N–H bond lengths and H–N–H angles were scattered in the region of 0.71–1.08 Å and 96°–119°, respectively, for phase II and 0.87–1.08 Å and 95°–123°, respectively, for phase III [6]. The differential Fourier synthesis of phase II showed that one well defined peak could be assigned as H4 ($\Delta\rho \approx 0.5$ eÅ^{-3}), other hydrogen atoms H1, H2 and H3 could correspond to three peaks among five weak peaks ($\Delta\rho \approx 0.3$ eÅ^{-3}) around N. Two-site disordered model for ammonium ion was not accepted as the reality and further ordered model was analyzed with four peaks among six ones to form a regular tetrahedron. However thermal parameters for hydrogen atoms H1 and H3 were significantly larger than ones for H2 and H4. The analysis of the result of differential Fourier synthesis and hydrogen thermal parameters led to the conclusion that ammonium ion in phase II is partially disordered. The differential Fourier synthesis of phase III exposed eight peaks with $\Delta\rho \approx 0.6$–0.8 eÅ^{-3} around two nitrogen atoms which could be eight hydrogen atoms. Thus ammonium ions in phase III must suit fully ordered model. The results of x-ray crystal structure study of phase II of LAS had not given definite presentation about orientational positions of ammonium ion.

1. EXPERIMENT AND RESULTS

There are two modifications of $LiNH_4SO_4$: α- and β-modifications which at room temperature have different crystal structures [7–9]. So the α-modification of LAS has space group $Pca2_1$ with Z = 8 and lattice parameters a = 10.196 Å, b = 4.991 Å and c = 17.100 Å [7, 8]. The β-polymorph belongs to space group $P2_1$cn with Z = 4 and lattice parameters a = 5.279 Å, b = 9.129 Å and c = 8.774 Å [8]. Both modifications are grown from aqueous solutions of $LiNH_4SO_4$ by

slow evaporation of water at the following temperatures: α-LAS at $T_{\rm gr}$ = 283 K and β-LAS at $T_{\rm gr}$ = 305 K [9] and at $T_{\rm gr}$ = 323 K [10].

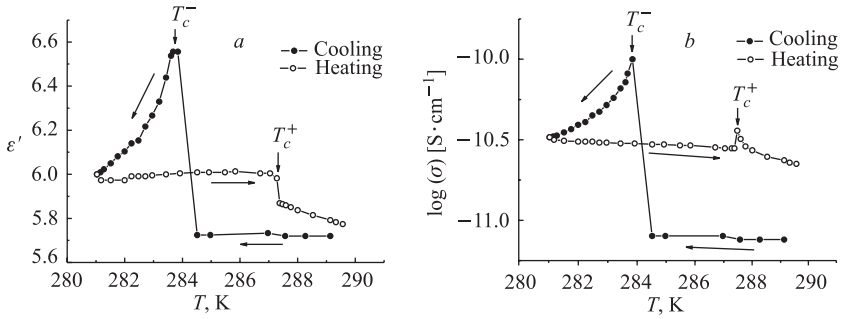

Fig. 1. The temperature dependences of dielectric permeability real part (a) and the conductivity (b) of $LiNH_4SO_4$ both on the frequency of 1 MHz

Table 1. The conditions of the experiment

Substance	β-$LiNH_4SO_4$	
Temperature	298 K	
Radiation	N	X-ray [6]
Wavelength	0.883(9) Å	0.71068 Å
Space group, Z	$P2_1cn$, Z = 4	$P2_1cn$, Z = 4
a	5.266(6) Å	5.282(1)
b	9.097(3) Å	9.131(3)
c	8.758(4) Å	8.780(2)
α	90°	90°
β	90°	90°
γ	90°	90°
Number of measured reflections	1929	2036
Number of independent reflections	858	1552
Number of variables	100	
R (|F|)	0.072	0.0362
wR (|Y|)	0.057	

The single crystal of LAS for recent investigations was grown by the evaporation of water from aqueous solution at $T_{\rm gr}$ = 313 K. The determination of the polymorph of the grown single crystal was carried out by the measurements of temperature dependences of dielectric permeability real part and the conductivity. For this purpose the silvery electrodes (Degussa paste) were applied on a single

Table 2. Atomic positions of β-$LiNH_4SO_4$, obtained by present neutron single crystal diffraction (N) and X-ray single crystal diffraction in [6]

Atom		x	y	z	Occupation
Li	N	0.2515(7)	0.0878(6)	0.3224(6)	1.0
	X-ray	0.2507(19)	0.0871(4)	0.3231(3)	
S	N	0.2507(9)	0.4166(4)	0.2026(4)	1.0
	X-ray	0.25(fixed)	0.41651(4)	0.20198(4)	
O1	N	0.2521(2)	0.4035(6)	0.0390(3)	1.0
	X-ray	0.2500(10)	0.4044(3)	0.0383(2)	
O2	N	0.3453(8)	0.2817(2)	0.2689(4)	1.0
	X-ray	0.3423(4)	0.2804(2)	0.2706(3)	
O3	N	–0.082(6)	0.4450(3)	0.2561(3)	1.0
	X-ray	–0.0096(3)	0.4459(2)	0.2567(2)	
O4	N	0.4176(8)	0.5374(2)	0.2504(3)	1.0
	X-ray	0.4151(4)	0.5382(2)	0.2502(2)	
N	N	0.7557(7)	0.2844(1)	0.4996(1)	1.0
	X-ray	0.7549(7)	0.2857(2)	0.5001(2)	
H1	N	0.8316(4)	0.1879(9)	0.5084(8)	1.0
	X-ray	0.835(18)	0.177(7)	0.506(8)	
H2	N	0.5773(6)	0.2666(5)	0.4839(4)	1.0
	X-ray	0.634(13)	0.295(5)	0.466(6)	
H3	N	0.8373(8)	0.3365(7)	0.4102(6)	1.0
	X-ray	0.844(18)	0.329(7)	0.424(9)	
H4	N	0.7887(9)	0.3466(7)	0.5939(6)	1.0
	X-ray	0.788(9)	0.340(4)	0.602(4)	

crystal sample prepared in the view of the flat parallel sheet with known area and thickness. The temperature dependences of dielectric characteristics were measured into air environment by LCR E7-21 measuring unit using the frequency of 1 MHz. The temperature hysteresis of measured phase transitions are suited to T_c^- = 284 K at cooling and to T_c^+ = 287 K at warming as that is presented in Fig. 1.

These temperature points are known for the phase transition from phase II into phase III for β-modification of $LiNH_4SO_4$. Thus it was shown that grown single crystal sample belongs to β-modification of $LiNH_4SO_4$.

The determination of the crystal structure of β-LAS is carried out by means of the single crystal neutron diffraction. The measurements of Bragg reflection intensities are fulfilled at room temperature from the sample with sizes $4\times4\times4$ mm^3 on E5 four circle neutron diffractometer set in BENSC HMI Ber II reactor (Berlin, Germany). The conditions of this experiment are presented in Table 1.

The atomic positions and thermal parameters are determined by the least-square method with the help of the XTal System [11]. Determined atomic positions in β-$LiNH_4SO_4$ are presented in Table 2.

Table 3. The anisotropic thermal parameters U_{ij} (Å^2) for phase II of LAS, defined as exp{–2π^2[U_{11}(ha*)^2+U_{22}(kb*)^2+U_{33}(lc*)^2+2U_{12}ha*kb*+2U_{13}ha*lc*+2U_{23}kb*lc*]}, are obtained by present neutron single crystal diffraction (N) and X-ray single crystal diffraction in [6]

Atom		U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Li	N	0.018(2)	0.016(2)	0.019(2)	–0.002(3)	–0.020(3)	0.010(2)
	X-ray	0.0225(11)	0.0222(11)	0.0220(11)	–0.0042(23)	–0.0052(31)	0.0007(11)
S	N	0.014(1)	0.013(1)	0.014(1)	0.004(1)	–0.002(2)	0.006(1)
	X-ray	0.0145(1)	0.0156(1)	0.0158(1)	0.0012(2)	0.0002(3)	0.0018(1)
O1	N	0.039(1)	0.119(4)	0.016(8)	–0.011(3)	0.002(2)	–0.007(2)
	X-ray	0.0418(9)	0.1205(18)	0.0162(5)	–0.0087(25)	–0.0032(18)	–0.0067(9)
O2	N	0.030(1)	0.015(8)	0.078(2)	0.007(9)	–0.005(4)	0.017(1)
	X-ray	0.0313(8)	0.0220(6)	0.0807(14)	0.0035(6)	–0.0066(10)	0.0206(7)
O3	N	0.018(7)	0.026(9)	0.036(1)	0.005(7)	0.009(8)	0.012(9)
	X-ray	0.0181(5)	0.0352(7)	0.0419(8)	0.0061(6)	0.0110(6)	0.0144(6)
O4	N	0.028(8)	0.019(8)	0.044(1)	–0.011(9)	0.015(9)	–0.012(9)
	X-ray	0.0317(7)	0.0264(6)	0.0474(9)	–0.0126(6)	–0.0160(7)	–0.0139(6)
N	N	0.029(6)	0.029(6)	0.022(5)	–0.003(8)	–0.017(7)	–0.001(5)
	X-ray	0.0296(7)	0.0301(6)	0.0237(6)	–0.0043(4)	0.0(13)	–0.0005(5)
H1	N	0.172(2)	0.055(3)	0.070(4)	0.044(7)	–0.008(7)	0.009(3)
	X-ray						
H2	N	0.048(4)	0.114(8)	0.104(7)	–0.029(5)	–0.002(4)	–0.049(6)
	X-ray						
H3	N	0.955(6)	0.057(3)	0.042(2)	–0.008(4)	0.018(4)	0.006(2)
	X-ray						
H4	N	0.081(6)	0.059(3)	0.043(2)	0.003(4)	–0.012(3)	–0.013(2)
	X-ray						

The obtained anisotropic thermal parameters of β-$LiNH_4SO_4$ by single crystal x-ray diffraction in [6] and by single crystal neutron diffraction in present study are assumed in Table 3 for the comparison.

Refined atomic positions from the results of neutron single crystal diffraction give the possibility to determine bond lengths for S–O(i), Li–O(i) and N–H(i) where $i = 1, \ldots, 4$. These calculated bond lengths are assumed in Table 4. The obtained mean bond lengths for S–O, Li–O and N–H by single crystal x-ray diffraction and single crystal neutron diffraction show that bond lengths for S–O and Li–O are similar independently of the radiation but mean bond lengths for N–H are different.

The crystal structure of β-$LiNH_4SO_4$ in accordance with atomic positions suited to phase II is presented in (ab) plane in Fig. 2 and in (bc) plane in Fig. 3.

Table 4. The determined bond lengths in β-$LiNH_4SO_4$ at room temperature (phase II)

Atoms	Bond lengths, Å	
	N	X-ray [6]
S–O1	1.438(4)	1.450(2)
S–O2	1.446(4)	1.461(2)
S–O3	1.465(6)	1.475(2)
S–O4	1.468(5)	1.472(2)
mean	**1.454**	**1.464**
Li–O1	1.899(5)	1.892(2)
Li–O2	1.891(6)	1.888(2)
Li–O3	1.939(8)	1.937(2)
Li–O4	1.926(9)	1.938(2)
mean	**1.914**	**1.914**
N–H1	0.968(1)	1.08(7)
N–H2	0.963(9)	0.71(7)
N–H3	1.011(7)	0.91(8)
N–H4	1.017(7)	1.04(4)
mean	**0.99**	**0.93**

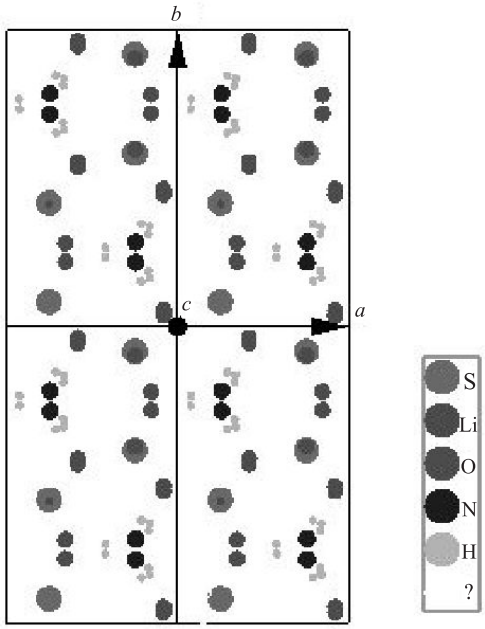

Fig. 2. The projection of the crystal structure of LAS (phase II) on (*ab*) plane

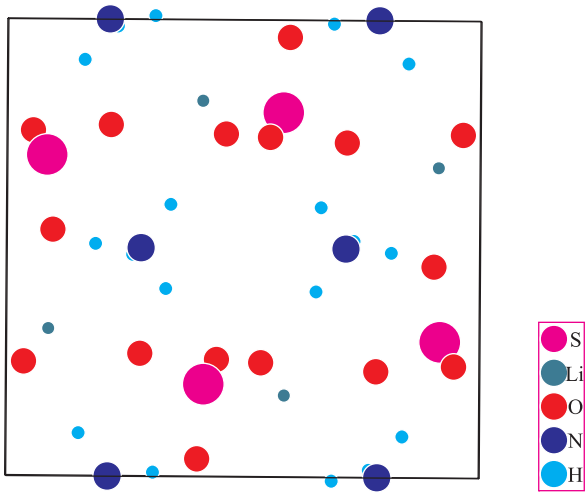

Fig. 3. The projection of the crystal structure of LAS (phase II) on (*bc*) plane

DISCUSSION AND CONCLUSIONS

The authors of x-ray study of crystal structure of phase II of LAS [6] did not present the anisotropic thermal parameters for hydrogen atoms but in the text it is pointed on very large isotropic thermal parameters for H1 and H3 hydrogen atoms.

However, anisotropic thermal parameters for hydrogen atoms, obtained in present single crystal neutron diffraction study of LAS in phase II, show indeed that U_{11} for hydrogen atoms H1 and H3 is significantly larger than for H2 and H4. The other anisotropic thermal parameters for all hydrogen atoms are approximately similar.

Significant result of single crystal neutron diffraction is concluded in the refinement of hydrogen positions in LAS phase II. These refined atomic positions give the possibility to determine with more accuracy the N–H bond lengths in comparison with the results of single crystal x-ray diffraction. If hydrogen positions obtained with the help of x-ray diffraction point to deformation of ammonium tetrahedra, then refined hydrogen positions with the help of neutron diffraction indicate that ammonium ions can be treated as regular tetrahedra.

The S–O and Li–O bond lengths obtained by single crystal x-ray and neutron diffraction have similar values.

Acknowledgements. The authors thank A. M. Balagurov for useful discussion and the Leading Scientific School of Prof. L. A. Shuvalov (Grant No НШ-1514.2003.2) for partial financial support.

REFERENCES

1. *Mitsui T. et al.* // J. Phys. Soc. Japan. 1975. V. 39. P. 845.
2. *Pepinsky R. et al.* // Phys. Rev. 1958. V. 111. P. 1467.
3. *Simonson T., Denoyer F., Moret R.* // J. Physique. 1984. V. 45. P. 125.
4. *Itoh K., Ishikura H., Nakamura E.* // Acta Cryst. B. 1981. V. 37. P. 664.
5. *Dollase W. A.* // Acta Cryst. B. 1969. V. 25. P. 2298.
6. *Mashiyama H., Kasano H.* // J. Phys. Soc. Japan. 1993. V. 62. P. 155.
7. *Lukaszewicz K., Pietraszko A.* // Pol. J. Chem. 1992. V. 66. P. 2057.
8. *Polomska M., Hilczer B., Baran J.* // J. Molec. Struc. 1994. V. 325. P. 105.
9. *Sosnowska I., Hilczer B., Piskunowicz P.* // Solid State Commun. 1990. V. 74. P. 1249.
10. *Gerbaux X. et al.* // Ferroelectrics. 1982. V. 40. P. 53.
11. The Gnu Xtal System User's Manual / Eds. Sydney Hall, Douglas du Boulay, and Roeli Olthof-Hazekamp. Crawley: University of Western Australia, 2002.

Received on September 9, 2005.

Редактор *Н. С. Скокова*

Подписано в печать 28.10.2005.
Формат 60 × 90/16. Бумага офсетная. Печать офсетная.
Усл. печ. л. 0,6. Уч.-изд. л. 0,8. Тираж 280 экз. Заказ № 55079.

Издательский отдел Объединенного института ядерных исследований
141980, г. Дубна, Московская обл., ул. Жолио-Кюри, 6.
E-mail: publish@pds.jinr.ru
www.jinr.ru/publish/