Institute for Theoretical
and Experimental Physics

25 – 02

ITEP-25-02

L.S.Smirnov, L.A.Shuvalov, M.L.Martinez
Sarrion, L.Mestres, M. Herraiz

FERMILAB
6 2004
LIBRARY

AMMONIUM ION BEHAVIOUR IN THE β-$LiRb_{1-X}(NH_4)_XSO_4$ MIXED CRYSTALS ($0.77<X<1.0$).

Moscow 2002

UDK 539.2 M16

AMMONIUM ION BEHAVIOUR IN THE β-$LIRB_{1-X}(NH_4)_XSO_4$ MIXED CRYSTALS (0.77<X<1.0): Preprint ITEP 25-02/

L.S.Smirnov, L.A.Shuvalov[1], M.L.Martinez Sarrion[2], L.Mestres[2], M. Herraiz[2] -M., 2002-

The study of the β-$LiRb_{1-x}(NH_4)_xSO_4$ mixed crystals carried out with the help of neutron powder diffraction and inelastic incoherent neutron scattering showed that the substitution of ammonium ions by rubidium stabilizes phase II from room temperature up to 20 K already at ammonium concentration x=0.91. At ammonium concentration x=0.77 the β-$LiRb_{1-x}(NH_4)_xSO_4$ mixed crystal at 20 K is found in orientational glass state. The mode with the energy near 200 cm^{-1} is absent at 20 K in generalized phonon density of states of phase II of the β-$LiRb_{1-x}(NH_4)_xSO_4$ mixed crystals and similar in orientational glass region.

ПОВЕДЕНИЕ ИОНОВ АММОНИЯ В СМЕШАННЫХ КРИСТАЛЛАХ β-$LIRB_{1-X}(NH_4)_XSO_4$ (0.77<X<1.0)

Л.С.Смирнов, Л.А.Шувалов[1], М.Л.Мартинец Саррион[2], Л.Местрес[2], М.Херраиз[2]

Исследование смешанных кристаллов β-$LiRb_{1-x}(NH_4)_xSO_4$, проведенное с помощью нейтронной порошковой дифракции и неупругого некогерентного рассеяния нейтронов, показало, что замещение ионов аммония рубидием стабилизирует фазу II от комнатной температуры до 20 К уже при концентрации аммония x=0.91. При концентрации аммония x=0.77 смешанный кристалл β-$LiRb_{1-x}(NH_4)_xSO_4$ при 20 К находится в состоянии ориентационного стекла. В обобщенной плотности фононных состояний фазы II, и аналогично в области ориентационного стекла, смешанных кристаллов β-$LiRb_{1-x}(NH_4)_xSO_4$ при 20 К отсутствует мода с энергией вблизи 200 $см^{-1}$.

Fig. – 6, Ref. – 18 names.

© Институт теоретической и экспериментальной физики, 2002

Работа выполнена при частичной финансовой поддержке Ведущей научной школы Л.А.Шувалова (грант № 00-15-96797) и Российского Фонда Фундаментальных Исследований (грант № 02-02-17330).

[1]. A.V.Shubnikov Institute of Crystallography RAS, Moscow, Russia
[2]. University of Barcelona, Barcelona, Spain
E-mail: lsmirnov@nf.jinr.ru

Introduction

The studies of physical properties and crystal structure investigations of ammonium lithium sulphate β-NH_4LiSO_4, called LAS, showed that this compound has following succession of phase transitions [1-7]:

phase I⇔459.5K⇔phase II ⇔283K⇔phase III ⇔27K⇔phase IV

The crystal structure of phase I is orthorhombic with space group Pmcn and lattice parameters at 478 K a=5.299(2) Å, b=9.199(2) Å, c=8.741(3) Å [1], the crystal structure of phase II is also orthorhombic with space group $P2_1cn$ [2,6] and lattice parameters at the temperature 298 K a=5.282(1) Å, b=9.131(3) Å, c=8.760(2) Å [6]. On the one hand the crystal structure of LAS is examined as a general tridymite structure [2]. On the other hand phase II of LAS is ferroelectric, phase transition I⇔II in LAS is similar to the para-ferroelectric phase transition in ammonium sulphate $(NH_4)_2SO_4$ (AS) and LAS is associated with the A'A''BX_4 family (where A', A''= Li, Na, K, Rb, Cs, NH_4, $N(CH_3)_4$, etc., and BX_4=SO_4, SeO_4, $ZnCl_4$, $ZnBr_4$, BeF_4, MoO_4, WO_4, etc.) [8]. The crystal structure of phase III is monoclinic with space group $P2_1/c11$ and lattice parameters at 190 K a=5.283(2) Å, b=9.121(5) Å, c=17.444(7) Å and β=90.00(4)° [6]. The crystal structure of phase IV is also monoclinic with space group Cc [7]. The crystal structures of phase II and phase III are presented in Figs. 1(a,b) which show that these structures are close to pseudohexagonal. X-ray results show that ammonium tetrahedrons are deformed, there is partial disorder of ammonium ions in phase II but perfect order in phase III [6].

It is known that the substitution of ammonium ions by rubidium ions in LAS can be accompanied by the change of the x-T phase diagram as shown in [9]. Presented here recent studies have examined the participation of ammonium ions in phase transitions and ammonium dynamics by inelastic incoherent neutron scattering (IINS) and neutron powder diffraction (NPD).

Experiment and results

The IINS and NPD spectra from LAS at 294, 260, 40, and 20 K were obtained by the time-of-flight method with the help of the NERA-PR neutron spectrometer (FLNP JINR, Dubna, Russia) [10]. The generalized phonon density of

states G(E) was calculated from the inelastic incoherent neutron scattering (IINS) spectra in one-phonon incoherent approximation with the program described in [11].

The neutron powder diffraction (NPD) spectra show that LAS undergoes phase transition:

phase II ⇔ phase III,

which is accompanied by the appearance of two new reflections with interplane distances 2.402 and 2.107 Å on NPD spectrum at 260 K in the comparison with NPD spectrum at 294 K as that is presented in Fig. 2. The NPD spectra of LAS measured at 40 and 20 K do not show noticeable difference which could confirm phase transition

phase III ⇔ phase IV

which must be at 27 K. Therefore we conclude that this transition was not observed because in accordance with [7] that is fulfilled fully only to 10 K.

The IINS spectra of LAS measured at these temperatures are presented in Fig. 3a. The generalised phonon densities of states G(E) calculated from these IINS spectra in one-phonon incoherent approximation are presented in Fig. 3b.

The IINS spectra contribute quasielastic incoherent neutron scattering (QINS) at 294 and 260 K which does not change during the phase transition II⇔III. However the cooling within the temperature region of the phase III is accompanied by a decrease of QINS which is undetected at 40 K. This behaviour can be described by the reorientation of ammonium ions. Ammonium anharmonicity decreases with cooling and leads to the appearance of fine structure of G(E) at 40 K. Small changes in G(E) between 40 and 20 K show the beginning of phase transition III⇔IV. The fine structure of G(E) allows measurement of the energies of the translational and librational modes of LAS in phase III. Comparisons of the results with those of other authors are presented in Table 1.

The translational modes (Σ) and the librational modes (ν_6^+) for ammonium ions were assigned on the basis of Raman scattering [13,14]. Since this technique produces higher resolution, the narrow lines from Raman spectra are shown together with the wide bands from the G(E) spectra in Table 1. Notice that the mode with energy 249 cm^{-1} on G(E) is absent from the data on neutron scattering in publication [12] and from the data on Raman scattering in publication [13].

The effect of the substitution of ammonium by rubidium on the succession of phase transitions was studied on β-$LiRb_{1-x}(NH_4)_xSO_4$ mixed crystals with the ammonium concentrations x=0.91 and 0.77 from 260 to 20 K on a NERA-PR neutron spectrometer. Phase transition II⇔III was absent (Fig. 4). The NPD spectra for $LiRb_{0.09}(NH_4)_{0.91}SO_4$ from 240 to 20 K, and for $LiRb_{0.23}(NH_4)_{0.77}SO_4$ at 20 K are similar to that for LAS at 294 K which is suitable for phase II. This observation shows that a rubidium concentrations of 0.09 and 0.23 stabilise phase II down 20 K.

The temperature evolution of the IINS spectra for $LiRb_{0.09}(NH_4)_{0.91}SO_4$ is presented in Fig. 5a and calculated G(E) for these temperatures are presented in Fig. 5b. The contribution of the QINS is observed in the IINS spectra of $LiRb_{0.09}(NH_4)_{0.91}SO_4$ at 240 and 200 K decreasing monotonically and is absent below 160 K. The G(E) spectrum of $LiRb_{0.09}(NH_4)_{0.91}SO_4$ at 240 K due to ammonium anharmonicity is presented in Fig. 5b by a broad maximum which starts to disintegrate on cooling. At 20 K G(E) has a fine structure which corresponds to phase II of mixed crystals.

The comparison of IINS and G(E) spectra of β-$LiRb_{1-x}(NH_4)_xSO_4$ mixed crystals is presented in Figs. 6a and 6b respectively. There is a difference between the phonon spectra of phase III of LAS and phase II of the $LiRb_{0.09}(NH_4)_{0.91}SO_4$ mixed crystal. The librational mode with energy near 200 cm^{-1} observed in phase III of LAS is almost absent in the phonon spectrum of mixed crystal with rubidium concentration x=0.09. The G(E) spectrum of the $LiRb_{0.23}(NH_4)_{0.77}SO_4$ at 20 K also corresponds to phase II but it is represented by broader maxima at similar energy positions than the G(E) spectrum for $LiRb_{0.09}(NH_4)_{0.91}SO_4$. This change shows that $LiRb_{0.23}(NH_4)_{0.77}SO_4$ can be in the orientational glass state at low temperature. The behaviour of the β-$LiRb_{1-x}(NH_4)_xSO_4$ mixed crystals is similar to the behaviour of the $[Rb_{1-x}(NH_4)_x]_3H(SO_4)_2$ mixed crystals [15] in which a rubidium concentration near 10% stabilizes phase II and at low temperature these mixed crystals are also in the orientational glass state.

Discussion

Obtained results about the ammonium ion behaviour in β-$LiRb_{1-x}(NH_4)_xSO_4$ mixed crystals are compared with those of other authors studied crystal structure by single crystal x-ray diffraction and nuclear magnetic resonance (NMR). .

As shown in [6] by x-ray single crystal diffraction study of crystal structure of phase II LAS the difference Fourier synthesis revealed more than four peaks around nitrogen, and a partially disordered ammonium ion crystal structure was proposed on basis of this observation. The IINS spectra of LAS at temperatures 294 and 260 K, which are suitable for phases II and III respectively, show that the contribution of QINS in IINS spectra does not have visible change through phase transition between these phases. Such temperature behaviour of the IINS spectra may be explained if the ammonium ions in the crystal structures of phases II and III do not change the reorientations about molecular axes, for example, C_2 and C_3 of ammonium tetrahedron or near crystallographic axes. However, in accordance with results of [6] in phase II LAS ammonium ions may reorient about crystallographic axes and phase transition II $\Leftrightarrow$ III is phase transition of type disorder-order. However, in this case the contribution of QINS in IINS spectra through the temperature of phase transition II $\Leftrightarrow$ III could be changed but this is not observed.

It is shown in [16], in the result of the analysis of NMR spectra ^7Li and ^2D of LAS in wide interval of the temperature, that ammonium ions are deformed and have electric dipole moments. The investigation by NMR of the spin-lattice relaxation times of LAS in the laboratory (T_1) and rotating ($T_{1\rho}$) frames from 400 to 77 K led authors [17] to conclude that they had observed phase transition near 133 K. Two discontinuities in the temperature dependence of both T_1 and $T_{1\rho}$ at 294 and 133 K defined three distinct temperature regions:

- from about 400 down to 294 K in region of phase II T_1 and $T_{1\rho}$ decrease with decreasing temperature with an activation energy of 1.9±0.1kcal/mole;
- then T_1 and $T_{1\rho}$ between 294 and 133 K decrease with decreasing temperature with an activation energy 2.55±0.05 kcal/mole;
- below 133 K $T_{1\rho}$ continues to decrease with activation energy 1.49±0.05 kcal/mole but T_1 goes through a minimum value at 115 K.

Authors of [17] showed that temperature dependence of T_1 and $T_{1\rho}$ can be explained by the reorientation of ammonium ions about molecular axes C_2 and C_3 and suggested that ammonium reorientation does not play a role in the phase transitions at 284 and 133 K.

The conclusion authors [17] about the reorientation of ammonium ions about molecular axes near phase transition II ⇔ III at 284 K is confirmed by IINS spectra above and below of this phase transition temperature (Fig. 3). However, the explanation of observed anomaly by these authors in LAS at 133 K can have other interpretation. The peculiarity observed in temperature dependence of T_1 may be the result of the change in ammonium ion reorientation when, with decreasing temperature inside the LAS crystal lattice, some potential barriers are increased and ammonium ions are not reoriented about any appropriate molecular axis. A similar anomaly in the temperature dependence of lattice parameters was observed in the monoclinic phase of NH_4SCN [18].

The analysis and comparison of physical properties of LAS obtained by abovemention methods gives us the possibility to propose the model of ammonium ion motion in this compound and the β-$LiRb_{1-x}(NH_4)_xSO_4$ mixed crystals.

The results of crystal structure investigation [6] and NMR studies [16,17] showed reorientation behaviour of ammonium ions but if on the base of [6] ammonium ions can reorient about crystallographic axes so on the base of [17] ammonium ions can reorient about molecular axes. The possibility of ammonium ions to reorientation about crystallographic axes in phase II can lead with cooling to the formation of orientational glass state. If ammonium ions are deformed and have electric dipole moments [16] and have the possibility to reorientation about molecular axes [17] then cooling of the β-$LiRb_{1-x}(NH_4)_xSO_4$ mixed crystals leads to the formation of dipolar orientational glass state. In order to understand in detail the nature of orientational glass state in the β-$LiRb_{1-x}(NH_4)_xSO_4$ mixed crystals it is necessary to carry out the refinement of the crystal structure of that with the help of

single crystal neutron diffraction. Earlier x-ray crystal structure study of phase II LAS [6] observed in the difference Fourier maps more than four peaks around nitrogen atoms which are suited to charge density distribution. However only neutron diffraction can determine real hydrogen nuclear density distribution and can help to answer on a question of real reorientations in crystal structure of phase II LAS.

Conclusion

The study of ammonium motion in β-$LiRb_{1-x}(NH_4)_xSO_4$ mixed crystals shows a significant influence of rubidium. This influence was examined by neutron powder diffraction and inelastic incoherent neutron scattering. The results of neutron diffraction from β-$LiRb_{1-x}(NH_4)_xSO_4$ mixed crystals with ammonium concentration x=1.0, 0.91 and 0.77 reveal the absence of the transition from phase II to phase III from 260 K to 20 K for x=0.91 and 0.77 and the stabilization of phase II due to the presence of rubidium.. The measured IINS spectra and calculated generalized phonon density of states G(E) for β-$LiRb_{1-x}(NH_4)_xSO_4$ mixed crystals reveal the change of ammonium ion dynamics. So the stabilized phase II of $LiRb_{0.09}(NH_4)_{0.91}SO_4$ does not have the mode near 200 cm^{-1} in the G(E) spectrum at 20 K by contrast to the G(E) spectrum for phase III of $LiNH_4SO_4$ at similar temperature. The broadening of peaks in the G(E) spectrum of $LiRb_{0.23}(NH_4)_{0.77}SO_4$ at 20 K testifies to the transition of this mixed crystal into region of orientational glass.

Acknowledgments.

We thank Dr.I.Natkaniec for useful discussions, S.I.Bragin for technical assistance, L.A.Shuvalov's school (grant № 00-15-96797) and Russian Fund for Basic Research (grant № 02-02-17330) for partial financial support.

Table 1. Energies of modes in β-NH_4LiSO_4 (energy in cm^{-1}).

Phase IV		Phase III			Assignment
G(E) 20K	NS 20K [12]	G(E) 40K	NS 40K [12]	Raman 126K [13]	
99.5	96 104	101	96	93 97 107 114 118 123	Σ
137	136	135	136	127 137	Σ
		150		148 155	Σ
168	160	168	168	169 175 179	Σ
184					Σ
207.4	200	206	200	202 210	ν_6^+
231		230		230	ν_6^+
248		249			ν_6^+
	272	271	272	270 280	ν_6^+
295					ν_6^+
353	344	352	360	342 356 365 369	ν_6^+
401	400	391		376 390 400 406	ν_6^+

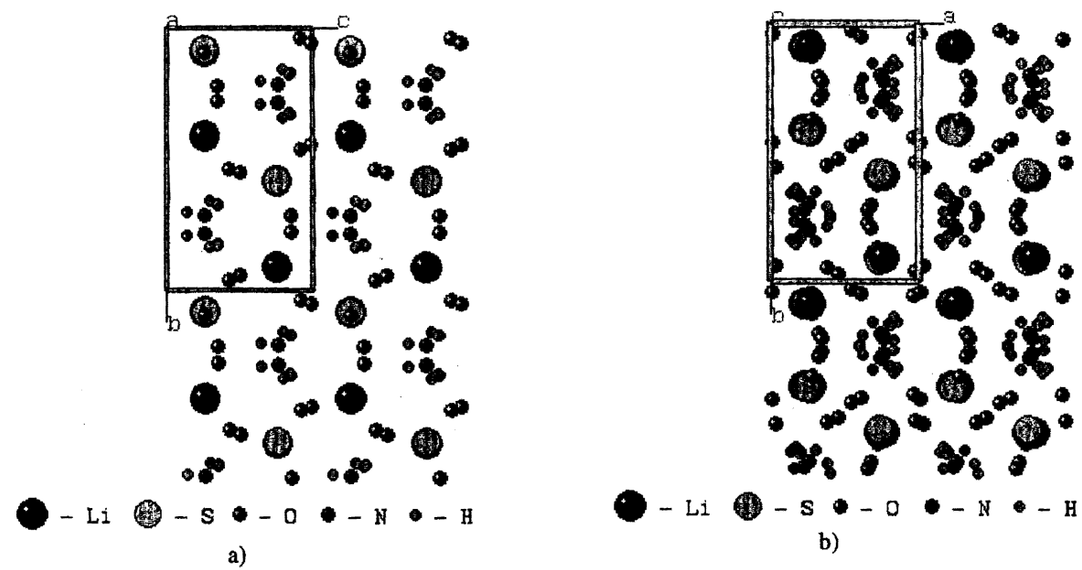


Fig. 1. The crystal structures of II (a) and III (b) phases of LAS.

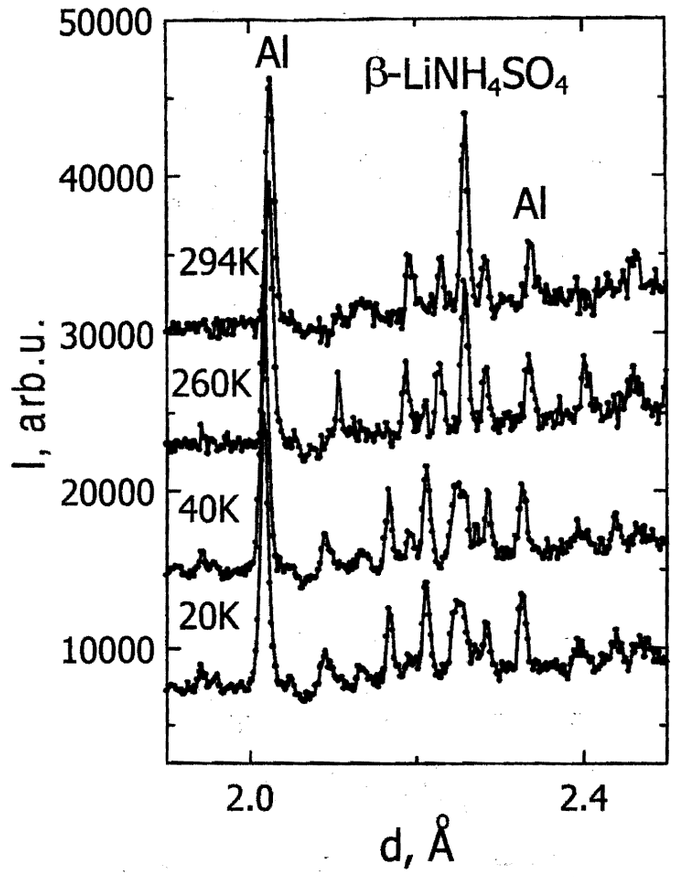


Fig. 2. The fragments of neutron powder diffraction spectra for β-$LiNH_4SO_4$ at different temperatures.

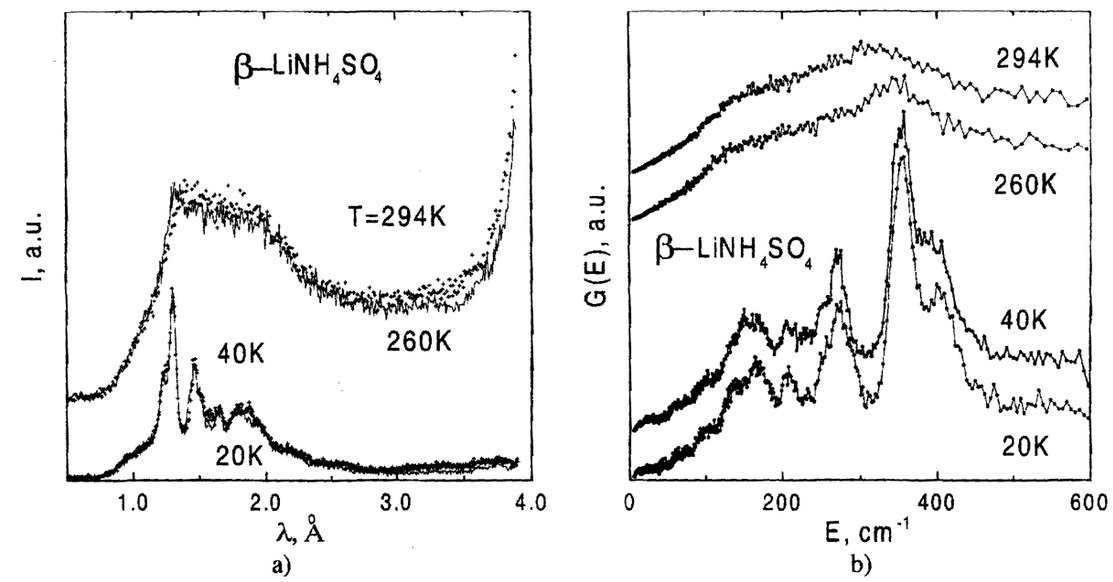


Fig. 3. The IINS spectra (a) and G(E) spectra (b) of LAS at different temperatures.

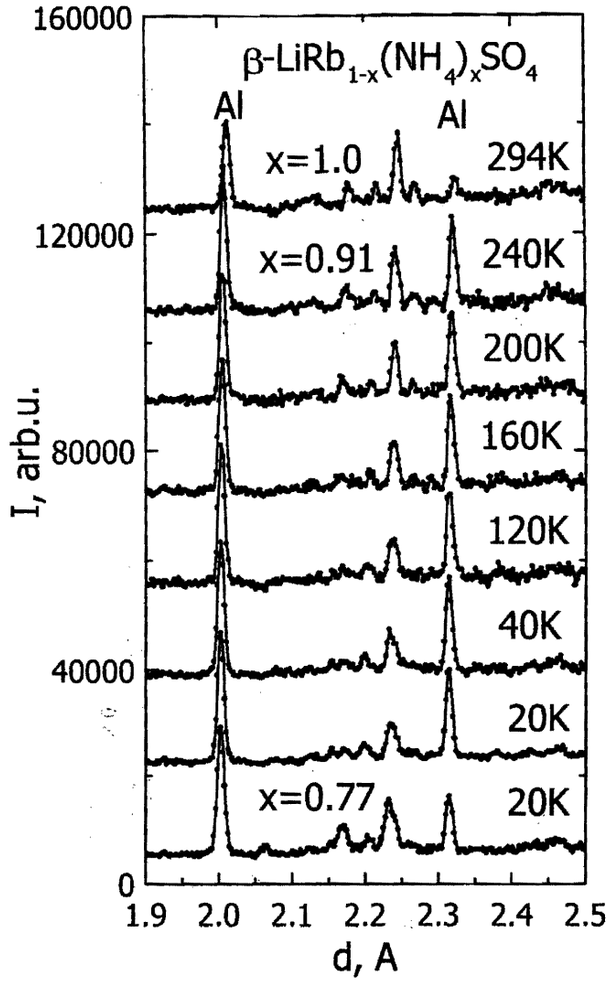
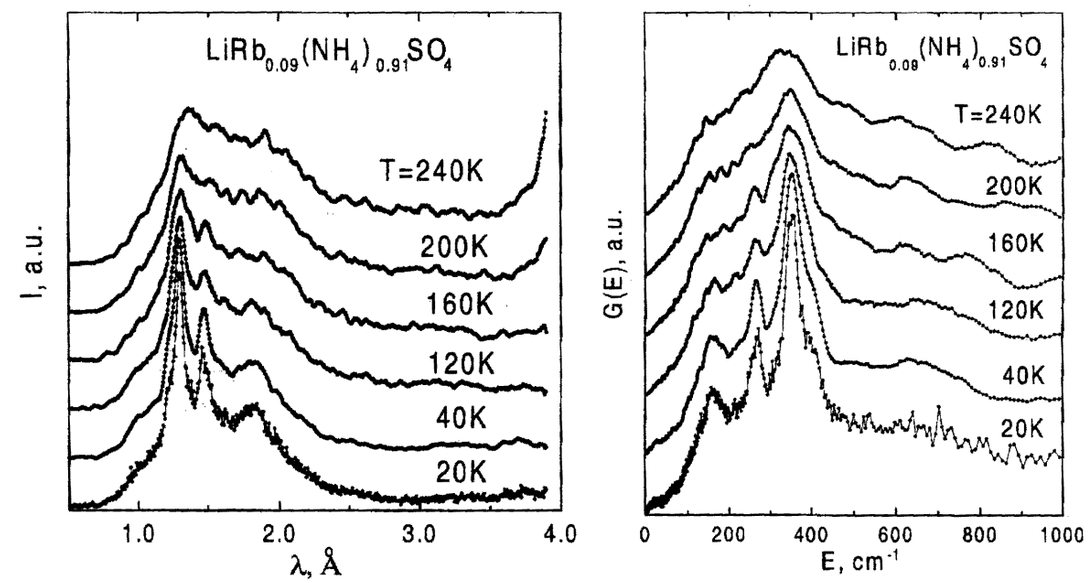


Fig. 4. The neutron powder diffraction spectra of β-$LiRb_{1-x}(NH_4)_xSO_4$ mixed crystals with x=0.77, 0.91 and 1.0 at different temperatures.



a) b)

Fig. 5. $LiRb_{0.09}(NH_4)_{0.91}SO_4$: (a)-the temperature dependence of the IINS spectra, (b)- the temperature dependence of the G(E) spectra.

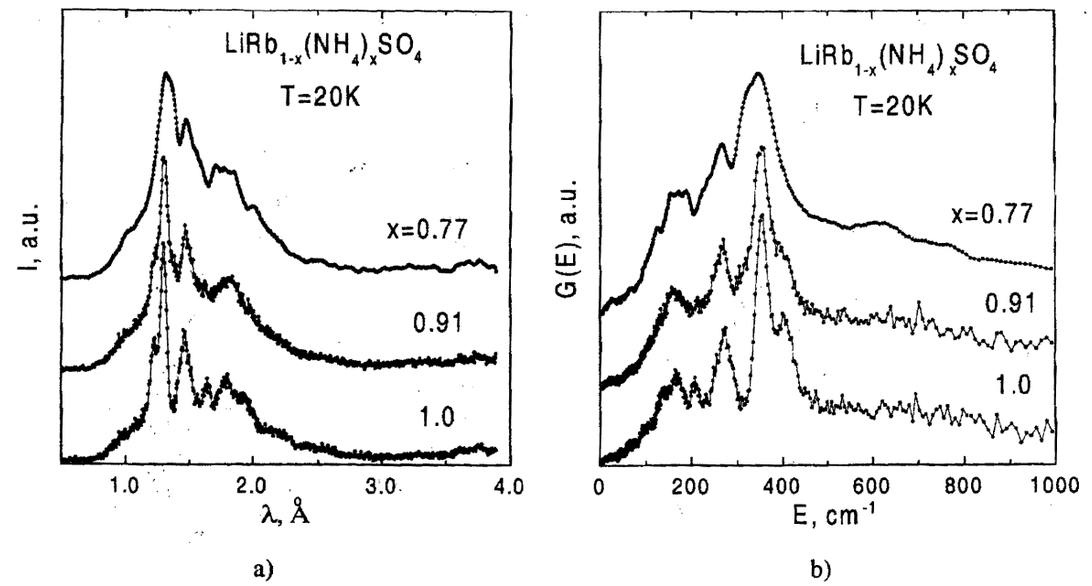


Fig. 6. The concentration dependence of (a)-the IINS spectra and (b)- the G(E) spectra of β-$LiRb_{1-x}(NH_4)_xSO_4$ at 20 K.

References
1. K.Itoh, H.Ishikura,E.Nakamura, Acta Crystallogr., **B37**, 664 (1981).
2. W.A.Dollase,Acta Crystallogr.**B25**, 2298 (1969).
3. K.S.Aleksandrov, I.P.Aléksandrova, L.I.Zherebtsova, A.I.Kruglik,, Izv.Akad.Nauk SSSR, Ser.Fiz. **39**, 943 (1975).
4. B.O.Hildman, Th.Hahn, L.E.Cross, R.E.Newnham, Appl.Phys.Lett., **27**, 103 (1975).
5. A.I.Kruglik, M.A.Simonov, K.S.Aleksandrov, Kristallografiya, **23**, 494 (1978).
6. H.Mashiyama, H.Kasano, J.Phys.Soc.Japan, **62**, 155 (1993).
7. T.Simonson, F.Denoyer, R.Moret, J.Physique, **45**, 125 (1984).
8. S.Aleksovska, S.C.Nyburg, Li.Pejov, V.M.Petrusevski, Acta Cryst., **B54**, 115 (1998).
9. K.Kawamura, A.Kuramashi, H.Nakamura, H.Kasanno, H.Mashiyama, S. Nakanishi, and H.Itoh, Ferroelectrics, **105**, 279 (1990).
10. I.Natkaniec, S.I. Bragin, J. Brankowski and J. Mayer. (1994). Multicrystal inverted geometry spectrometer NERA-PR at the IBR-2 pulsed reactor. In U. Steigenberger, T. Brome, G. Rees and A. Soper (Ed), Proceedings of the ICANS XII Meeting, Abingdon 1993, RAL Report No. 94-025, Vol. I, pp. 89-96.
11. E.L.Bokhenkov I. Natkaniec and E.F. Sheka. Sov. Phys. JETP, **43,** 536 (1976).
12. I.Sosnowska, J.Sosnowski, M.Prager, Phonons 89. Editors S.Hunklinger, W.Ludwig, G.Weiss, World Scientific, v.**1**, 148 (1990).
13. Yu.I.Yuzyuk, V.I.Torgashev, I.Gregora, A.H.A.H.Fuith, J.Phys.:Condens. Matter, **11**, 889 (1999).
14. P.Kumara Acharya, P.S.Narayanan, Indian J.Pure&Appl.Physics, **11**, 514 (1973).
15. L.S.Smirnov, A.I.Baranov, L.A.Shuvalov, L.Bobrowicz-Sarga, I.Natkaniec, S.Waplak, FTT, **43**, 115 (2001).
16. K.S.Aleksandrov, I.P.Aleksandrova, A.T.Anistratov, V.F.Shabanov, Izv.Akad.Nauk SSSR, Ser.Fiz. **41**, 599 (1977).
17. A.Watton, E.C.Reynhardt, H.E.Petch, J.Chem.Phys., **69**, 1263 (1978).
18. M.Dlouha, S.Vratislav, I.Natkaniec, L.S.Smirnov, Krystallografiya, **43**, 237 (1998).

Л.С.Смирнов, Л.А.Шувалов, М.Л.Мартинец Саррион, Л.Местрес, М.Херраиз
Поведение ионов аммония в смешанных кристаллах β-$LiRb_{1-x}(NH_4)_xSO_4$ ($0.77<x<1.0$)

Подписано к печати 28.12.02 Формат 60 × 90 1.16
Усл.-печ.л. 0,62 Уч.-изд.л.0,5 Тираж 101 экз. Заказ 25
Индекс 3649

Отпечатано в ИТЭФ, 117259, Москва, Б.Черемушкинская, 25