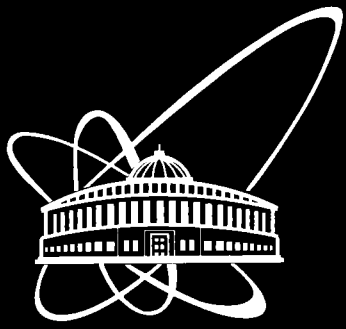

ОБЪЕДИНЕННЫЙ
ИНСТИТУТ
ЯДЕРНЫХ
ИССЛЕДОВАНИЙ

Дубна

E17-2002-281

NEUTRON SCATTERING INVESTIGATIONS OF THE PROPERTIES OF THE $x-T$ PHASE DIAGRAM OF $Rb_{1-x}(NH_4)_xI$ MIXED CRYSTALS

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I. Introduction

Studies of the x-T phase diagram of $Rb_{1-x}(NH_4)_xI$ mixed crystals is of significance for the understanding of possible effects of inner strains. During the last decade the x-T phase diagram of $K_{1-x}(NH_4)_xI$ mixed crystals was studied in detail. It is shown that the observed peculiarities of the system at low temperatures could be explained as being due to inner strains whose appearance is caused by difference in the ionic radii of potassium and ammonium [1-6]. This difference can be responsible for the appearance of an ε-phase with a new crystal structure on the x-T phase diagram of $K_{1-x}(NH_4)_xI$ mixed crystals.

Usually, KI do not undergo any phase transitions up to low temperatures. NH_4I , however, undergoes a series of phase transitions at being cooled [7, 8]:

$$\alpha\text{-phase} \Leftrightarrow 255.4K \Leftrightarrow \beta\text{-phase} \Leftrightarrow 231.4K \Leftrightarrow \gamma\text{-phase.}$$

The crystal structure of these phases was investigated by x-ray and neutron diffraction [9, 10]. The cubic α-phase is described by the space group $Fm3m\text{-}O_h^5$ with Z=4, ammonium ions are disordered in this phase. The cubic β-phase is described by the space group $Pm3m\text{-}O_h^1$ with Z=1, ammonium ions are also disordered in this phase. The tetragonal γ-phase is an ordered structure of ammonium ions described by the space group $P4/nmm\text{-}D_{4h}^7$ with Z=2.

The x-T phase diagram of $K_{1-x}(NH_4)_xI$ at low temperature is presented by the following series of phases as a function of ammonium concentration:

$$KI \Leftrightarrow \alpha\text{-phase} \Leftrightarrow OG\ (\textit{orientational glass}) \Leftrightarrow \varepsilon\text{-phase} \Leftrightarrow \beta\text{-phase} \Leftrightarrow \gamma\text{-phase} \Leftrightarrow NH_4I.$$

There is practically no difference between the ionic radii of rubidium and ammonium. RbI and KI are isomorphic and RbI does not have phase transitions from room to lower temperatures, and so does KI. RbI and NH_4I form solid solutions at room temperature over the entire ammonium concentration region [11]. We present the results of neutron powder diffraction and inelastic incoherent neutron scattering studies of the peculiarities of the x-T phase diagram of $Rb_{1-x}(NH_4)_xI$ carried out to observe the ε-phase and shift of phase boundaries as compared to the x-T phase diagram of $K_{1-x}(NH_4)_xI$ mixed crystals.

II. Experiments and results

The investigated powder samples of $Rb_{1-x}(NH_4)_xI$ mixed crystals with the different ammonium concentrations were prepared by slow evaporation of liquid solutions having the corresponding stoichiometric content. The concentrations in the obtained powder samples were controlled by special chemical methods and x-ray phase analysis.

The crystal structure of $Rb_{1-x}(NH_4)_xI$ mixed crystals and the dynamics of ammonium ions were studied by the neutron powder diffraction (NPD) and inelastic incoherent neutron scattering (IINS) methods. This complex method of investigation of the properties of $Rb_{1-x}(NH_4)_xI$ mixed crystals allows carrying out a more complete study of x-T phase diagram peculiarities through search of general dependence between the crystal structure and lattice dynamics and structural relaxation of separate lattice units. In the case of $Rb_{1-x}(NH_4)_xI$ mixed crystals, it is possible to investigate the effect of ammonium disorder on the crystal structure and ammonium dynamics in crystal structures with the different types of order by IINS methods.

II a. Diffraction measurements

The refining of the crystal structure of $Rb_{1-x}(NH_4)_xI$ mixed crystals as a function of ammonium concentration and temperature was done by carrying out measurements on the NERA-PR spectrometer and DN-12 diffractometer (IBR-2, JINR, Dubna) by the TOF method [12,13] and on the diffractometer of the steady reactor (CTU, Rzez) by a conventional method [14]. The x-T phase diagram of $Rb_{1-x}(NH_4)_xI$ mixed crystals was studied using specimens with the ammonium concentration x=0.01, 0.02, 0.06, 0.10, 0.16, 0.29, 0.40, 0.50, 0.66 and 0.77 in the temperature interval from room temperature to 10 K.

The neutron diffraction experiments were performed on the DN-12 diffractometer at the IBR-2 high flux pulsed reactor (Dubna, Russia) [13]. The volume of the sample was approximately 20 mm^3. The scattering angle was $2\theta = 45^0$. The spectrometer resolution is $\Delta d/d=0.022$ at d=2 Å. A special cryostat constructed on the base of a closed cycle helium refrigerator was used to create low temperatures on sample. A typical exposition time for each temperature point was almost 3 h.

The cross sections of the x-T phase diagram of $Rb_{1-x}(NH_4)_xI$ mixed crystals as a function of ammonium concentration and as a function of temperature were studied at low temperatures between 10-20 K and at several ammonium concentrations, respectively. The results of the study of the x-T phase diagram of $Rb_{1-x}(NH_4)_xI$ mixed crystals with NPD are illustrated in figures. The NPD results as a function of ammonium concentration at T=20 K obtained with the NERA-PR spectrometer are shown in Fig. 1.

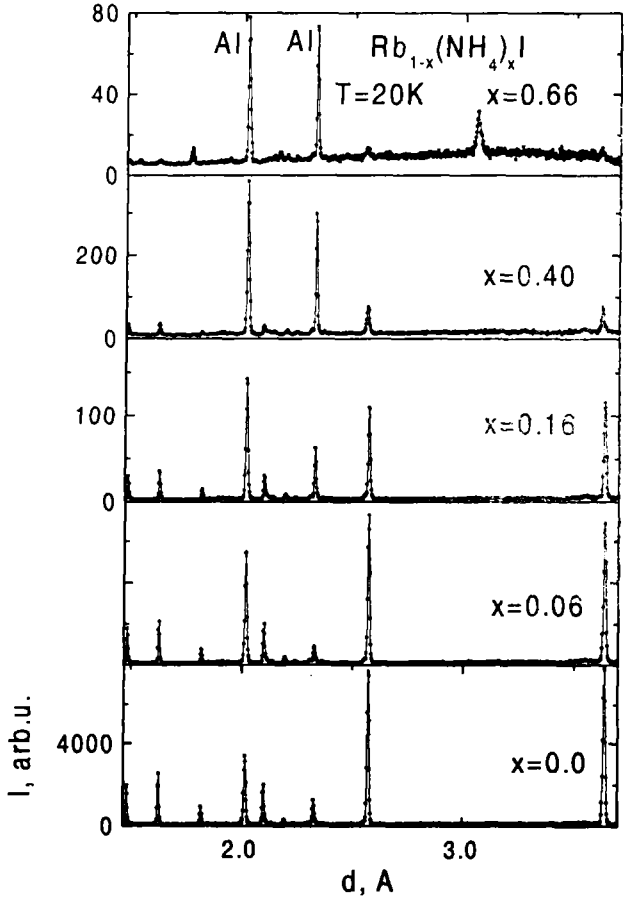

Fig. 1. The NPD spectra of $Rb_{1-x}(NH_4)_xI$ (x=0.0; 0.06; 0.16; 0.40; 0.66) mixed crystals obtained with the NERA-PR spectrometer.

It is seen that for x=0.0, 0.06, 0.16 and 0.40 the crystal structure of the $Rb_{1-x}(NH_4)_xI$ mixed crystals has a long-rang order and is found in the α-phase. It is worth noting that the transition from α-phase to β-phase does not have an expressed boundary and is observed within the concentration region ~0.50<x<0.66 where the α- and β-phase are observed together (in Fig. 1 the diffraction spectrum for x=0.50 is not shown). The crystal structure of $Rb_{1-x}(NH_4)_xI$ mixed crystal with the ammonium concentration

x=0.66 is described by a long-rang order which suits the β-phase. For the sample with x=0.66 the NPD spectrum has a small volume of the α-phase.

Samples of $Rb_{1-x}(NH_4)_xI$ mixed crystals with the ammonium concentration x=0.29, 0.40, 0.66 and 0.77 were studied at room and lower temperatures with the DN-12 diffractometer. The refinement of the powder neutron diffraction patterns was made, as a rule, by the program MRIA [15]. The examples of some obtained NPD spectra for x=0.29 and 0.77 and the results of the treatment by the profile method of Rietveld are presented in Fig. 2(a,b). The experimental points, calculated profile and the difference curve are shown. The observed effects of ammonium concentration and temperature on the lattice parameters of $Rb_{1-x}(NH_4)_xI$ mixed crystals are shown in Fig. 3 (a-c).

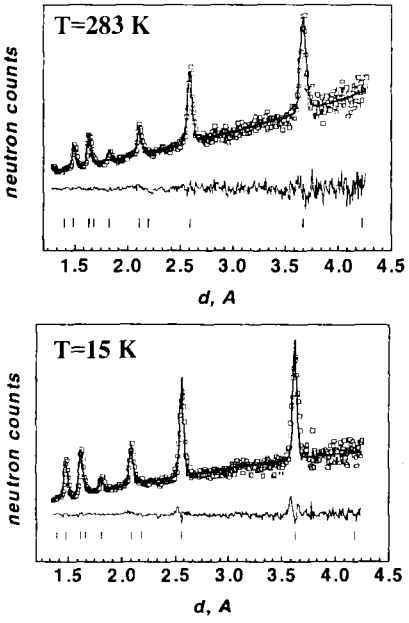

Fig. 2 (a). The diffraction patterns of $Rb_{0.71}(NH_4)_{0.29}I$ at 283 K (sp.gr. Fm3m) and 15 K (sp.gr. Fm3m)

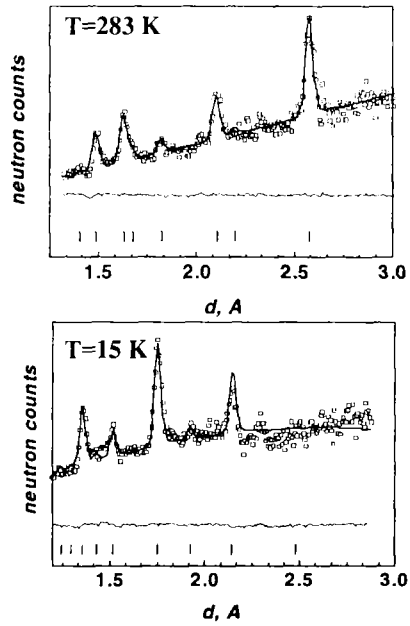

Fig. 2 (b). The diffraction patterns of $Rb_{0.23}(NH_4)_{0.77}I$ at 283 K (sp.gr. Fm3m) and 15 K (sp.gr. Pm3m)

The refinement of the crystal structure of $Rb_{1-x}(NH_4)_xI$ mixed crystals carried out with the CTU diffractometer was done for the ammonium concentration x= 0.01, 0.02, 0.06, 0.10, 0.16, 0.40 and 0.66 over a wide temperature interval of 10 to 300 K.

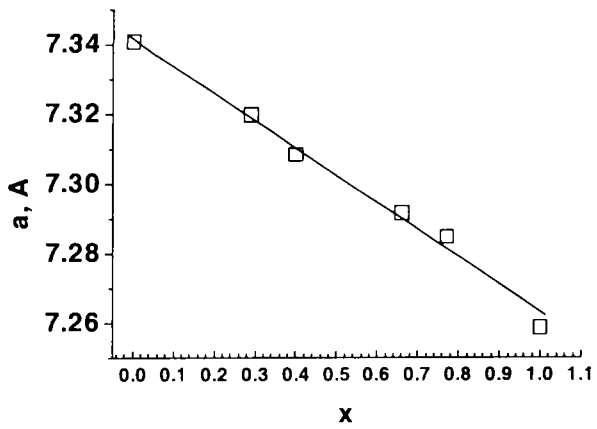

Fig. 3(a). *The lattice parameters of $Rb_{1-x}(NH_4)_xI$ mixed crystals as a function of NH_4^+-concentration at room temperature.*

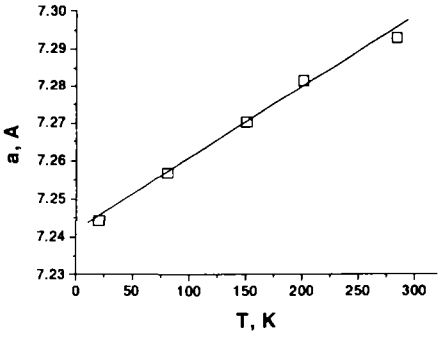

Fig. 3 (b). *The lattice parameter a of the cubic structure of $Rb_{0.71}(NH_4)_{0.29}I$ mixed crystals as a function of temperature.*

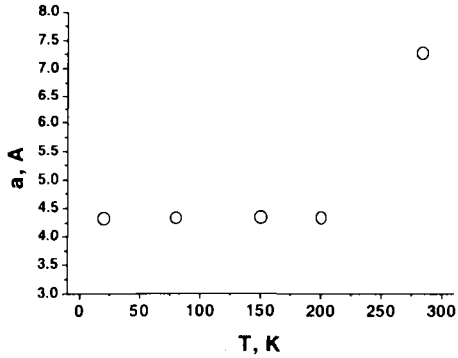

Fig.3 (c). *The lattice parameter a of the cubic structure of $Rb_{0.23}(NH_4)_{0.77}I$ mixed crystals as a function of temperature.*

Processing of the obtained NPD spectra by the Rietveld method allowed the atomic positions in $Rb_{1-x}(NH_4)_xI$ mixed crystals to be determined as a function of ammonium concentration and temperature. The results are summarized in Table 1.

Table 1. Atomic positions of hydrogen atoms in $Rb_{1-x}(NH_4)_xI$ mixed crystals as a function of ammonium concentration and temperature

x	0.29	0.40	0.66	0.77
T	280K			
Sp.Gr.	Fm3m	Fm3m	Fm3m	Fm3m
H1-32(f)-(x)	0.5710(8)	0.5703(9)	0.5743(2)	0.5743(7)
H2-96(k)-(x,z)	0.5164(7)	0.5164(7)	0.525(5)	0.5367(9)
	0.3672(3)	0.3651(6)	0.3421(3)	0.3549(6)
T	200K			
Sp.Gr.	Fm3m			
H1-32(f)-(x)	0.5689(5)			
H2-96(k)-(x,z)	0.5140(2)			
	0.3604(6)			
T	150K			
Sp.Gr.	Fm3m			
H1-32(f)-(x)	0.5689(5)			
H2-96(k)-(x,z)	0.5140(2)			
	0.3504(9)			
T	15K			
Sp.Gr.	Fm3m			Pm3m
H-8(g)-(x)				0.3685(8)
H1-32(f)-(x)	0.5627(8)			
H2-96(k)-(x,z)	0.5140(2)			
	0.3604(9)			

II b. Measurements by inelastic neutron scattering

The IINS spectra of $Rb_{1-x}(NH_4)_xI$ mixed crystals were measured by the TOF method on the NERA-PR inverted geometry spectrometer (IBR-2, JINR, Dubna) [16]. The NERA-PR spectrometer allows the measurement of IINS spectra in the interval of energy transfer up to 150 meV using pirolitic graphite crystal-analyzers whose resolution is 0.6 meV for the wavelength λ_0=4.15 Å.

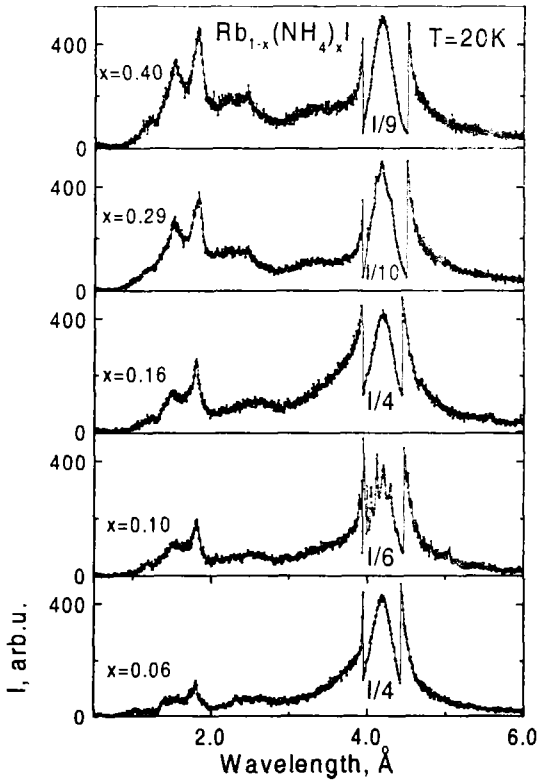

Fig. 4 (a). The IINS spectra of $Rb_{1-x}(NH_4)_xI$ mixed crystals at 20 K.

The dynamics of ammonium in $Rb_{1-x}(NH_4)_xI$ mixed crystals was studied in the concentration section of the x-T phase diagram at low temperature T=20 K for the samples with x=0.01, 0.02, 0.06, 0.10, 0.16, 0.29, 0.40, 0.50 and 0.66. The obtained intensities of the IINS spectra for several ammonium concentrations are presented in Fig. 4 (a,b). The IINS spectra for the ammonium concentrations at 20 K presented in Fig. 4(a) show the presence of a strong contribution of quasielastic incoherent neutron scattering (QINS) to the wings of the elastic profile from the crystal-analyzers centered at wavelength λo=4.15 Å. The contribution of QINS depends on the ammonium concentration in the following way. The QINS contribution increases with increasing ammonium concentration at x=0.06, 0.10, 0.16. Then, starting from the ammonium concentration x=0.29 and for x=0.40 the QINS contribution decreases and the contribution of low energy modes appears to be sharper. The observed concentration dependence of IINS spectra can be explained in the following way.

$Rb_{1-x}(NH_4)_xI$ mixed crystals with the ammonium concentration x=0.06, 0.10, 0.16 are found within a disordered α-phase and the QINS contribution suits ammonium ions reorientations. An increase in the ammonium concentration is due to changes in the the altitude of the reorientation barrier as a result of the rise of the ammonium-ammonium interaction. This leads to changes in the short-range order between ammonium ions, which starts to play a dominant role in the formation of the orientational glass state. Thus, $Rb_{1-x}(NH_4)_xI$ mixed crystals with the ammonium concentrations x=0.29 and 0.40 are found on the x-T phase diagram in the region of the orientational glass state.

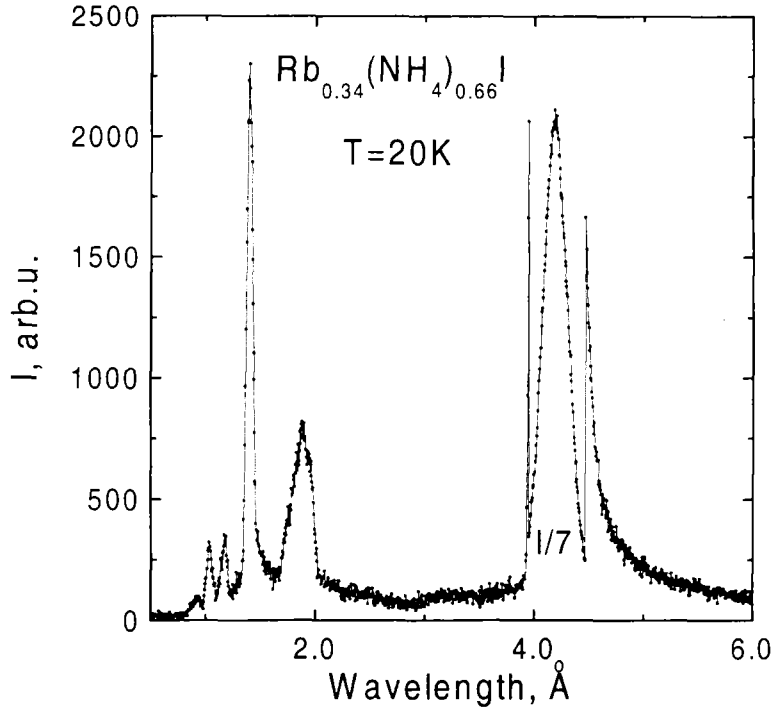

Fig. 4(b). The IINS spectrum of a $Rb_{0.34}(NH_4)_{0.66}I$ mixed crystal at 20 K.

The results of the diffraction study show that for this concentration region the long-range order could suit the cubic crystal structure with the space group Fm3m. However, the short-range order makes the crystal structure more complex in this concentration region due to formation of the orientational glass state. Superstructure

reflections are not, however, observed in the obtained powder neutron diffraction spectra in this concentration region.

No QINS contribution is observed in the IINS spectrum for $Rb_{0.34}(NH_4)_{0.66}I$ mixed crystals which are found to contain the α- and β-phase at 20K. The ammonium ions in the crystal structure of the β-phase are disordered, but no QINS contribution is from the sample with such structure. This observation points to a low frequency of ammonium reorientation in the β-phase at low temperature which is why the resolution of the NERA-PR spectrometer does not make it possible to observe such behavior of ammonium ions.

II c. Generalized phonon density of states

Usually, the measured IINS spectra can be converted to the generalized phonon density of state G(E) in the one-phonon incoherent approximation [17]. The G(E) spectra of $Rb_{1-x}(NH_4)_xI$ mixed crystals at 20 K are shown in Fig. 5 for the concentrations x=0.0, 0.06, 0.16, 0.40 and 0.66.

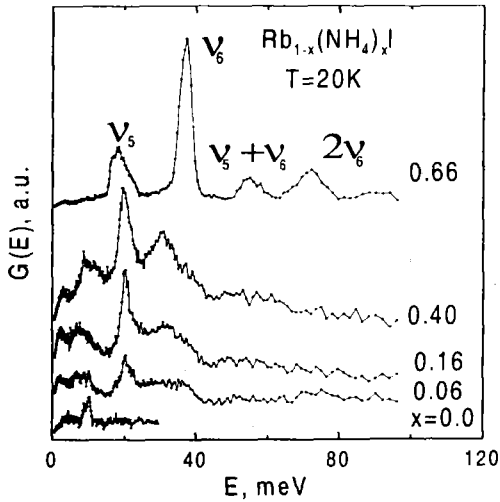

Fig. 5. The generalized phonon densities of states G(E) of $Rb_{1-x}(NH_4)_xI$ mixed crystals at 20 K.

A comparison of the presented G(E) spectra shows the appearance of additional modes in mixed crystals with energies larger than the energy of the optical mode in RbI. Such modes in mixed crystals are called local modes and they are associated with ammonium dynamics. The mode with the energy ~20 meV is an ammonium

local translational optical mode which is marked v_5 and that with the energy ~30 meV is an ammonium local librational mode which is marked v_6. The G(E) spectra for the ammonium concentrations x=0.06, 0.16 and 0.40 have modes with the energy ~2.5 and 10 meV that are not observed in RbI but are found on a continuous phonon spectrum of RbI. These modes will be named the resonance modes E_r^1 and E_r^2, respectively. The resonance and local modes are only observed in $Rb_{1-x}(NH_4)_xI$ mixed crystals at low temperature within the concentration region on the x-T phase diagram corresponding to the disordered α-phase and orientational glass state phase. The resonance modes are absent at 20 K in the G(E) spectrum of $Rb_{1-x}(NH_4)_xI$ mixed crystals with the concentration x=0.66 which is found within the β-phase. It is worth noting that there were observed Raman modes for $Rb_{1-x}(NH_4)_xI$ mixed crystals in the β-phase at 20 K, namely v_5+v_6 and the second harmonic of the librational mode $2v_6$, which are not observed in a mixed crystal within the α-phase.

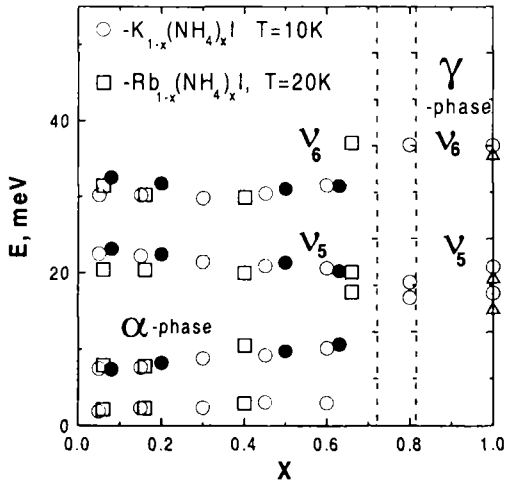

Fig. 6. The comparison of the observed energies of modes in $K_{1-x}(NH_4)_xI$ and $Rb_{1-x}(NH_4)_xI$ mixed crystals at low temperature.

III. Conclusion

The use of a complex neutron scattering method involving neutron powder diffraction and inelastic incoherent neutron scattering provides a wider possibility of detail investigations. Recent neutron scattering studies have made it possible to determine the concentration region of existence of the orientational glass state, which is difficult to do through just powder diffraction methods according to this report. The

obtained results allow some conclusions to be made about the properties of the x-T phase diagram of $Rb_{1-x}(NH_4)_xI$ mixed crystals. The results show:

a) $Rb_{1-x}(NH_4)_xI$ mixed crystals are found in the α-phase over the entire concentration region $0.0<x<1.0$ at room temperature;

b) the long-range order with the crystal structure of the α-phase is conserved over the ammonium concentration region up to $x=0.29$ at temperatures from room to 20 K;

c) $Rb_{1-x}(NH_4)_xI$ mixed crystals with $x=0.77$ are found to have a long-range order of the β-phase at low temperature which changes to the α-phase at temperatures between 200 and 280 K;

d) the phase transition from crystal structure with the α-phase to crystal structure with the β-phase does not havea sharp boundary and is as follows:
α-phase ($0.01\leq x\leq 0.16$) ⇔OG ($0.29\leq x\leq 0.40$) ⇔ α-phase+β-phase ($0.50\leq x\leq 0.66$) ⇔ β-phase ($x=0.77$);

e) the investigation of the crystal structure of $Rb_{1-x}(NH_4)_xI$ mixed crystals with NPD shows the absence of the concentration region with a crystal structure similar to the ε-phase earlier observed in $K_{1-x}(NH_4)_xI$ mixed crystals.

The x-T phase diagram of $Rb_{1-x}(NH_4)_xI$ mixed crystals for a full concentration region of ammonium ions is not present in this report. The determination of the concentration region of the β- and γ-phase continues. There is also a problem of the existence of the ε-phase on the x-T phase diagram of $Rb_{1-x}(NH_4)_xI$ mixed crystals. The absence of the ε-phase in $Rb_{1-x}(NH_4)_xI$ mixed crystals could be explained by the absence of inner strains. It is worth noting that the energy of the librational mode of ammonium ions in the ε-phase is closed to the energy of the librarional ammonium mode in the α-phase and is different from the energy of the librational ammonium mode in the β- and γ-phases. This difference in the energies of librational ammonium ions is due to the different number of near-lying surrounding iodide atoms. The ammonium ion only interacts with 6 atoms of I in the α- and ε-phase but not with 8 iodide atoms as in the β- and γ-phases. However, a search of the ε-phase in the system of $Rb_{1-x}(NH_4)_xI$ mixed crystals should continue using single crystal neutron diffraction and the history of the discovery of the ε-phase in $K_{1-x}(NH_4)_xI$ mixed crystals points to the necessity of such investigations.

Acknowledgments

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Нейтронографическое исследование фазовой диаграммы смешанных кристаллов $Rb_{1-x}(NH_4)_xI$

Смешанные кристаллы $Rb_{1-x}(NH_4)_xI$ исследовались с помощью порошковой нейтронной дифракции и неупругого рассеяния нейтронов в области концентраций аммония $0{,}01 < x < 0{,}77$ в диапазоне температур от 15 до 300 K. Установлено, что при концентрации $x = 0{,}50$ и $x = 0{,}66$ при понижении температуры происходит структурный фазовый переход из α-фазы в β-фазу. Неупругое рассеяние нейтронов указывает на существование состояния ориентационного стекла для области концентраций аммония $0{,}29 < x < 0{,}40$.

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Препринт Объединенного института ядерных исследований. Дубна, 2002

Smirnov L. S. et al.
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Neutron Scattering Investigations of the Properties of the $x-T$ Phase Diagram of $Rb_{1-x}(NH_4)_xI$ Mixed Crystals

The $x-T$ phase diagram of $Rb_{1-x}(NH_4)_xI$ is studied using samples with the ammonium concentration $0.01 < x < 0.77$ over a wide temperature region of 15 to 300 K by neutron powder diffraction and inelastic incoherent neutron scattering. The results of powder diffraction studies show that at low temperatures a phase transition from α-phase to β-phase is observed at ammonium concentrations $x = 0.50$ and $x = 0.66$. Inelastic incoherent neutron scattering detects a region of the orientational glass state at ammonium concentrations $0.29 < x < 0.40$.

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

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