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STUDY OF AMMONIUM MOLECULAR ION  
IMPURITY MODES IN  $\text{Rb}_{1-x}(\text{NH}_4)_x\text{I}$  MIXED CRYSTALS  
BY INELASTIC INCOHERENT NEUTRON SCATTERING

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Смирнов Л. С. и др. Изучение примесных мод молекулярного иона аммония в смешанных кристаллах $Rb_{1-x}(NH_4)_xI$ с помощью неупругого некогерентного рассеяния нейтронов	E14-2010-108
<p>Изучение динамики аммония в смешанных кристаллах <math>Rb_{1-x}(NH_4)_xI</math> проведено с помощью неупругого некогерентного рассеяния нейтронов в концентрационной области ориентационно разупорядоченной <math>\alpha</math>-фазы <math>0,0 &lt; x &lt; 0,40</math> при температурах от 2 до 150 К. Наблюдаемые резонансные моды соответствуют трем диапазонам энергии: 0,19–0,481 (I), 0,56–3,0 (II) и 4,0–10,0 (III) мэВ. Моды диапазона I могли бы быть описаны как вращательные туннельные моды мультипольных моментов ионов аммония. Моды в области диапазона энергии II соответствуют вычисленным вращательным туннельным энергиям между расщепленными уровнями основного либрационного уровня иона аммония. Моды диапазона III могут быть описаны как локальные щелевые моды иона аммония, потому что они расположены между акустической и оптической зонами плотности фононных состояний в RbI.</p> <p>Работа выполнена в Лаборатории нейтронной физики им. И. М. Франка ОИЯИ.</p> <p>Сообщение Объединенного института ядерных исследований. Дубна, 2010</p>	

Smirnov L. S. et al. Study of Ammonium Molecular Ion Impurity Modes in $Rb_{1-x}(NH_4)_xI$ Mixed Crystals by Inelastic Incoherent Neutron Scattering	E14-2010-108
<p>The study of ammonium dynamics in <math>Rb_{1-x}(NH_4)_xI</math> mixed crystals was carried out by inelastic incoherent neutron scattering in the concentration region of orientationally disordered <math>\alpha</math>-phase, <math>0.0 &lt; x &lt; 0.40</math>, at temperature range from 2 to 150 K. The observed resonance modes correspond to three energy regions: 0.19–0.481 (I), 0.56–3.0 (II) and 4.0–10.0 (III) meV. The modes of region I could be described by rotational tunneling energies of the multipole moments of ammonium ions. The modes within energy region II correspond to the calculated rotational tunneling energies between splitted levels of the ground librational level of ammonium ion. The modes of region III can be described as local gap modes of ammonium ion because they are located between acoustic and optic branches of RbI phonon density of states.</p> <p>The investigation has been performed at the Frank Laboratory of Neutron Physics, JINR.</p> <p>Communication of the Joint Institute for Nuclear Research. Dubna, 2010</p>	

## INTRODUCTION

The  $\text{Rb}_{1-x}(\text{NH}_4)_x\text{I}$  mixed crystals form a continuous sequence of solid-state solutions throughout the whole concentration region from room temperature down to 2 K [1]. The  $x$ - $T$  phase diagram of these  $\text{Rb}_{1-x}(\text{NH}_4)_x\text{I}$  mixed crystals was determined by powder neutron diffraction. Analysis of the powder diffraction spectra showed that at 20 K the system is found in an FCC-type orientationally disordered crystal lattice (or the  $\alpha$ -phase) up to an ammonium concentration of  $x = 0.40$  [1, 2].

Early dynamic studies into the minimization of the inner strain of the  $\text{Rb}_{1-x}(\text{NH}_4)_x\text{I}$  mixed crystals were carried out by virtue of the fact that the  $\text{Rb}^+$  and  $\text{NH}_4^+$  ionic radii are almost the same. First measurements, fulfilled on NERA-PR spectrometer (FLNP JINR, Dubna, Russia), showed that at 20 K the dynamics of the mixed crystals is represented by two low-energy modes and local translational ( $\nu_5$ ) and librational ( $\nu_6$ ) modes [1, 2]. A possible explanation for the observed low-energy modes is provided by the rotational tunneling modes studied in different ammonium alkali-metal halide lattices [3–8].

In order to identify the observed low-energy modes more precisely,  $\text{Rb}_{1-x}(\text{NH}_4)_x\text{I}$  mixed crystal dynamics was studied using inelastic incoherent neutron scattering (IINS) across a wider energy transfer range as a function of ammonium concentration and temperature.

### 1. SHORT REVIEW OF INELASTIC NEUTRON SCATTERING THEORY FROM MIXED CRYSTALS WITH MOLECULAR IMPURITIES

The development of the theory of mixed crystal dynamics was started in the early '60s of last century. The theory of the mixed crystal dynamics for substitutions by monatomic impurities firstly was presented by I. M. Lifshitz in 1942 [I. M. Lifshitz. Nuovo Cimento 3, Suppl. A1, 716 (1956)]. It was shown that resonance or local modes appear in crystal-host due to the alterations in mass and force constants. However, if in the case of monatomic impurity the mixed crystal has only translational degree of freedom, then in the case of a molecular impurity center the crystal-host is presented by translational and orientational degrees of freedom. M. Wagner [17] developed the method how orientational

coordinates can be excluded by means of molecular Green's function and the Lifshitz method can be applied to the remaining unchanged number of lattice coordinates.

There is now an additional effective disturbance which has poles at the molecular frequencies via molecular Green's function. These poles will produce new sharp resonances if they lie within the phonon bands.

The abstract formalism for general problem is outlined by M. Wagner in [18].

The time-independent equations of motion of «molecular system» in lattice-host can be written as

$$[L + A(\omega^2) - \omega^2 I]z + B\zeta = 0 \quad (3N \text{ equations}), \quad (1a)$$

$$(\alpha - \omega^2 I)\zeta + \bar{B}z = 0 \quad (3s \text{ equations}), \quad (1b)$$

where  $z$  is the set of mass-reduced Cartesian lattice coordinates, and  $\zeta$  is the set of molecular coordinates (center of mass excluded and mass-reduced).  $L$  is suited to the matrix of undisturbed lattice,  $A(\omega^2)$  matrix describing the disturbance, both are  $3N \times 3N$  matrixes.  $B$  describes the interaction between the molecular and lattice coordinates ( $3N \times 3s$  matrix), and  $\alpha$  is the  $3s \times 3s$  molecular matrix.

M. Wagner proposed to solve the system of equations (1a), (1b) in the following way. Without the disturbance  $A$  and the coupling  $B$  each equation from the system (1a), (1b) goes to system of the following two Green's functions:

$$(L - \omega^2 I)^{-1} = G(\omega^2) = \sum_{k\lambda} \frac{z(k\lambda)z(k\lambda)}{\omega_{k\lambda}^2 - \omega^2}, \quad (2a)$$

$$(\alpha - \omega^2 I)^{-1} = \gamma(\omega^2) = \sum_k \frac{\varsigma(k)\varsigma(k)}{\omega_k^2 - \omega^2}, \quad (2b)$$

where  $z(k\lambda)$ ,  $\varsigma(k)$  are eigenvectors and,  $\omega_{k\lambda}^2$ ,  $\omega_k^2$  are eigenfrequencies of matrix  $L$  and  $\alpha$ , respectively.

The property of equations (1a), (1b) permits excluding of molecular coordinates in the form

$$\zeta = -\gamma(\omega^2)\bar{B}z, \quad (3)$$

from equation (1a) we have the equation

$$z = -G(\omega^2)[A(\omega^2) - B\gamma(\omega^2)\bar{B}]z. \quad (4)$$

Equation (4) arrives as a determinantal equation on eigenfrequencies

$$D(\omega^2) = \text{Det} [I + g(\omega^2)[a(\omega^2) - b\gamma(\omega^2)\bar{b}]] = 0 \quad (5)$$

of rank  $3r$ ,  $g(\omega^2)$  is  $3r \times 3r$  matrix in  $G(\omega^2)$  matrix, which are calculated on  $r$  involved lattice points.  $a$  and  $b$  are matrix elements of  $A$  and  $B$  matrices, which are written as

$$A = \begin{pmatrix} a & 0 \\ 0 & 0 \end{pmatrix} \text{ and } B = (b, 0), \quad (6)$$

where  $a$  is  $3r \times 3r$  and  $b$  is  $3r \times 3s$  matrices, both spread out only over  $r$  lattice points around molecular ions involved in disturbance.

Thus, initial Lifshitz's matrix  $I + g(\omega^2)a$  is refilled by additional matrix —  $g(\omega^2)b\gamma(\omega^2)\bar{b}$ . The solution of determinantal equation (5) arrives at the determination of the influence of molecular impurity modes on phonon spectrum of crystal-host and the formation of phonon spectrum of mixed crystal.

M. Wagner [18], analyzing the behavior of molecular impurity center in crystal-host, noticed that the molecule in mixed crystal can be found in several different equilibrium orientations. The flips from one potential well to the other by means of the tunneling can split up each eigenstate of the single well into a band of energy levels. The molecule can accomplish transitions between splitted levels inside of one band for account of phonon scattering. Thus there is the probability of new resonance scattering in the low-energy region.

The development of mixed crystal dynamics with molecular impurities demands to carry out the consideration for concrete molecule and to take into account the angular momentum of eigenstates for librating molecule, which can tunnel between several equivalent orientations divided by potential barriers.

The equations of the moving for the system of molecular defects coupling with the lattice are presented as follows [19]:

$$(\omega^2 - D)U + (\lambda/M)X = 0, \quad (7a)$$

$$(\lambda/M)U + (\omega^2 - \omega_o^2)X = 0. \quad (7b)$$

Here  $U$  and  $X$  are mass-reduced phonon and inherent modes of molecular center, respectively.  $D$  — dynamical matrix of the ideal crystal-host,  $M$  — the mass of crystal-host,  $\omega$  — the frequency of inherent mode of the molecular defect,  $\lambda/M$  — the vector of coupling coefficients between molecular defect and lattice. The exclusion of inherent mode coordinates  $X$  from Eq.(7a) leads to formal determinant:

$$[\omega^2 - D - \lambda\lambda(\omega^2 - \omega_o^2)^{-1}M^{-2}]U = 0. \quad (8)$$

The form of this equation  $(\omega^2 - D - \Delta)U = 0$  is met in the theory for substitution impurities without inherent degrees of freedom. But here  $\Delta$  has resonance denominator  $1/(\omega^2 - \omega_o^2)$ , leading to the hybridization of phonons with inherent modes of molecular defect which can significantly increase the effect of the lattice-impurity coupling. The phonon disturbance by molecular defect

can be observed in some cases by the method of inelastic neutron scattering. The quantitative estimations [19–21] show the existence of two extreme cases, which determine the hybrid splitting of coupled modes in two approximations of small and large damping, presented in Fig. 1, *a*, *b*.

The phonon Green's function,  $G(\vec{q}j; \nu)$ , determined as Fourier transform of retarded correlation functions displacement–displacement for the crystal with small concentration of impurities has the following expression [22]:

$$G(\vec{q}j; \nu) = \frac{1}{\nu^2 - \nu^2(\vec{q}j) - ct(\vec{q}; \nu)},$$

where  $\nu(\vec{q}j)$  —phonon frequency of the crystal with wave vector,  $\vec{q}j$ ,  $t(\vec{q}j; \nu)$  — scattering matrix for single impurity. The scattering matrix is determined by expression  $t = \Delta/(1 - G_0\Delta)$  for the impurity which produces the disturbance  $\Delta$ , and  $G_0$  is Green's function of crystal-host. Now this Green's function can be used for the presentation by the known rules of two different neutron scattering laws: inelastic coherent neutron scattering (ICNS) and inelastic incoherent neutron scattering (IINS) [22].

There are results of experimental investigations which obtained the explanation based on the above-mentioned theory. This has the relation to the study of phonon spectrum of the  $(\text{KCl})_{1-x}(\text{CN})_x$  mixed crystal [23], in which the hybridization of phonon and librational modes was observed by means of the inelastic coherent neutron scattering (ICNS). The hybridization of phonon and librational modes in the  $\text{K}(\text{Cl}_{1-x}\text{CN}_x)$  mixed crystal happens in accordance with the approximation of small damping, presented in Fig. 1, *a*.

The influence of the Frenkel pair on the phonon spectrum for irradiated Cu may be the other example [24]. The disturbance of the transverse phonon branch along the direction of wave vector  $\vec{q} = (0, 0, \zeta)2\pi/a$  in the irradiated Cu was

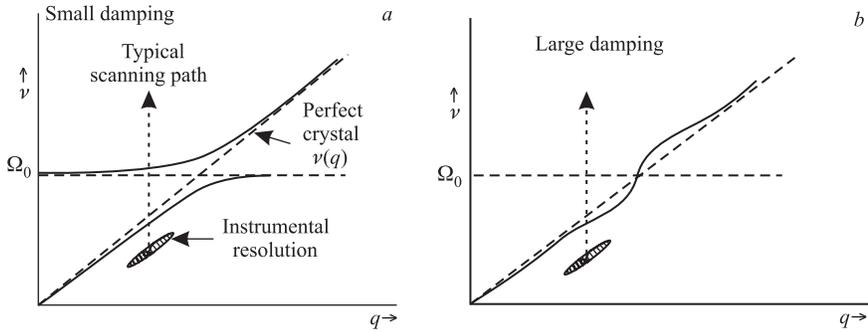


Fig. 1. Two types of hybridization between phonons and the inherent mode of a complex defect: *a*) small damping, *b*) large damping [21]

observed by means of ICNS in accordance with the theory of large damping presented in Fig. 1, *b* [24], which happens for account of the coupling of phonon mode with librational mode of the Frenkel pair.

The study of the dynamics of the  $\text{Rb}_{1-x}(\text{NH}_4)_x\text{I}$  mixed crystals was carried out by means of the inelastic incoherent neutron scattering from powder crystals. In this case the IINS intensity is measured as a function of the energy transfer with summing up all phonon momentum transfer and presents the information about phonon density of states. Thus observed peaks in the IINS intensity in the region of low-energy transfer present the inelastic neutron scattering from phonon modes and inherent modes of molecular impurity.

## 2. EXPERIMENTAL RESULTS

The powder samples of  $\text{Rb}_{1-x}(\text{NH}_4)_x\text{I}$  were prepared as follows. The starting iodide compounds were of analytical reagent grade. Solid solutions with the general formula  $\text{Rb}_{1-x}(\text{NH}_4)_x\text{I}$  were obtained by mixing  $\text{NH}_4\text{I}$  and  $\text{RbI}$  in varying stoichiometric proportions in aqueous solution and thermostating them at 40 °C. Polycrystalline samples were obtained through slow evaporation. Chemical analyses were carried out. Nitrogen and hydrogen contents were determined in a Carlo Erba EA 1108 microanalyzer. Rubidium content was determined using a Philips PV 9200X atomic absorption spectrophotometer. Iodide content was determined by titration. For phase analysis by X-ray powder diffraction Siemens D500 automatic diffractometer was used ( $\text{Cu K}\alpha$  radiation with a scan speed of  $1/20 \text{ min}^{-1}$  in a  $2\Theta$  range of 10–80°). The iodide starting phases were confirmed to be phase-pure through XRD patterns in agreement with those reported in the literature. The XRD results for the binary system showed that single phase solid solutions had been formed. Their XRD patterns were indexed by analogy with ammonium iodide and their lattice parameters were calculated using the AFFMAIL program. The instrument was calibrated with silicon as an external standard before and after measurements.

The experimental studies of the dynamics of  $\text{Rb}_{1-x}(\text{NH}_4)_x\text{I}$  mixed crystals in the  $\alpha$ -phase by IINS were carried out on different spectrometers, at two different nuclear reactors in different energy transfer diapasons. The measurements of the IINS spectra in the energy transfer region  $1.0 < E < 50.0 \text{ meV}$  were carried out on the NERA-PR neutron spectrometer at the IBR-2 high-flux pulsed reactor (FLNP JINR, Dubna, Russia) at temperature of 20 K.

The measurements in the energy transfer regions  $-4.5 < E < 4.5$  and  $-1.0 < E < 1.0 \text{ meV}$  were carried out on the IN5, and in the energy transfer region  $-2.0 < E < 2.0 \text{ meV}$  on the IN6, time-of-flight high resolution neutron spectrometers at the ILL high-flux reactor (ILL, Grenoble, France) at temperature range from 2 to 150 K.

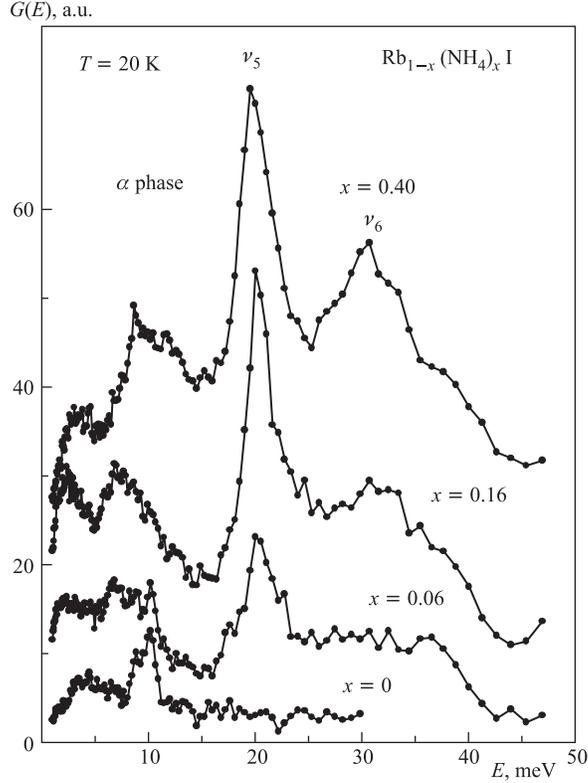


Fig. 2. The  $G(E)$  spectra of  $\text{Rb}_{1-x}(\text{NH}_4)_x\text{I}$  mixed crystals at 20 K, measured on the NERA-PR spectrometer

The IINS spectra, obtained on the NERA-PR spectrometer, were transformed to the  $G(E)$  phonon density of state using the one-phonon incoherent approximation. The  $G(E)$  spectra were separated with the help of the decomposition of spectrum profiles on the series of peaks described by Gaussians. This was performed for the  $\text{Rb}_{1-x}(\text{NH}_4)_x\text{I}$   $G(E)$  spectra for  $x = 0.0, 0.06, 0.16$  and  $0.40$  at 20 K as a function of energy transfer from 1 to 50 meV. The  $G(E)$  spectra of  $\text{Rb}_{1-x}(\text{NH}_4)_x\text{I}$  mixed crystals are presented in Fig. 2.

The  $G(E)$  spectrum of clear  $\text{RbI}$  presents two bands, acoustic and optic phonons, with energies of 4.69 and 9.78 meV, respectively. The  $G(E)$  spectra for mixed crystals with  $x = 0.06$  and  $0.16$  are described by two low-energy modes, named also resonance modes, that are set within the phonon spectrum of  $\text{RbI}$  host-crystal, and local translational ( $\nu_5$ ) and librational ( $\nu_6$ ) modes. Phonon spectrum

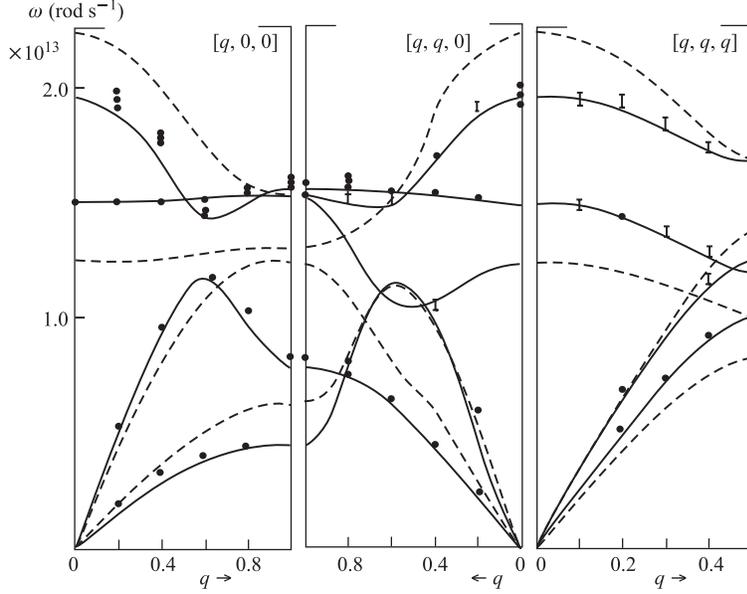


Fig. 3. Dispersion phonon curves of RbI at room temperature [9]

for RbI was studied experimentally by inelastic coherent neutron scattering [9], and obtained dispersion phonon modes are presented in Fig. 3.

Dispersion phonon curves show the gap between acoustic and optic modes in directions [100] and [110] of Brillouin zone and the intercrossing acoustic and optic modes near the boundary of Brillouin zone in the direction [111]. The energies of local modes  $\nu_5$  and  $\nu_6$  are more than the maximum cut-off energy of the clear RbI phonon spectrum [9].

The  $G(E)$  spectrum for  $\text{Rb}_{0.60}(\text{NH}_4)_{0.40}\text{I}$  at 20 K is found in the orientational glass state, the dynamics of which is represented by acoustic and optic modes and local translational ( $\nu_5$ ) and librational ( $\nu_6$ ) modes (Fig. 2).

The measurement of low-energy resonance modes on the NERA-PR spectrometer is limited by its resolution function ( $\Delta E = 0.66$  meV). Therefore, the measurements of the IINS spectra of the  $\text{Rb}_{1-x}(\text{NH}_4)_x\text{I}$  mixed crystals must be carried out on a spectrometer with a better resolution function. Measurements for  $\text{Rb}_{0.64}(\text{NH}_4)_{0.36}\text{I}$  mixed crystal were carried out on the IN5 spectrometer at temperature range from 5 to 60 K. The IN5 neutron monochromatic beam with  $\lambda_0 = 3.5$  Å allowed observations of the low-energy mode with 2.57 meV at 5 K in the energy transfer regions  $-4.5 < E < 4.5$  meV. This was close to the low-energy mode with 2.25 meV observed on the NERA-PR spectrometer at 20 K

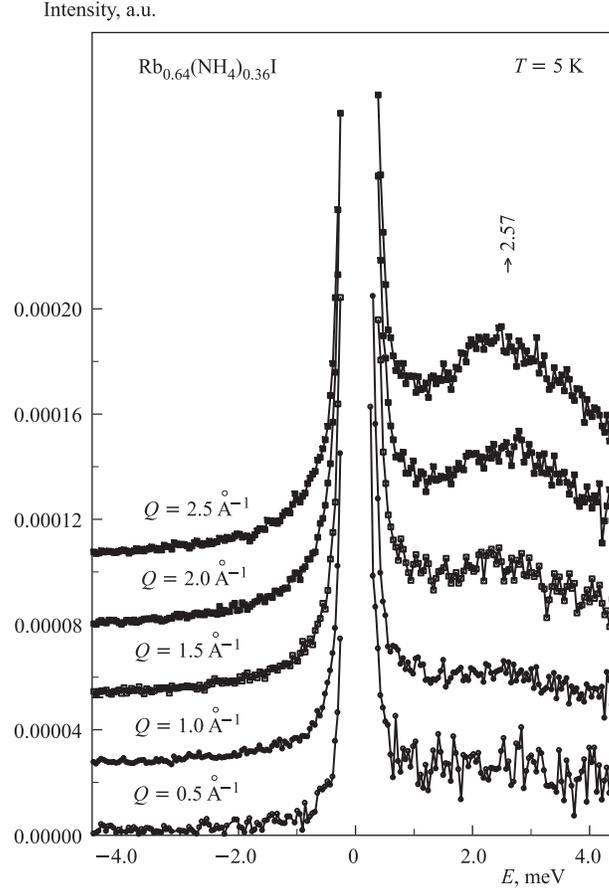


Fig. 4. The IINS spectra for  $\text{Rb}_{0.64}(\text{NH}_4)_{0.36}\text{I}$  mixed crystal at the temperature 5 K for different scattering vector  $Q = 0.5, 1.0, 1.5, 2.0$  and  $2.5 \text{ \AA}^{-1}$  (ILL IN5 spectrometer,  $\lambda_0 = 3.5 \text{ \AA}$ )

for mixed crystal with  $x = 0.16$ . Then the influence of the temperatures from 5 to 60 K on the IINS intensity from  $\text{Rb}_{0.64}(\text{NH}_4)_{0.36}\text{I}$  was determined on the IN5 spectrometer; results are presented in Fig. 4.

The use of a monochromatic neutron beam with the wavelength  $\lambda_0 = 5.12 \text{ \AA}$  (resolution  $\Delta E = 0.1 \text{ meV}$ ) on the IN6 spectrometer gives the possibility to carry out the measurements of the IINS spectra in the energy transfer region  $-2.0 < E < 2.0 \text{ meV}$ . The IINS spectra from the  $\text{Rb}_{1-x}(\text{NH}_4)_x\text{I}$  mixed crystals with  $x = 0.01, 0.02, 0.06, 0.16, 0.40$  were measured, and the low-energy modes

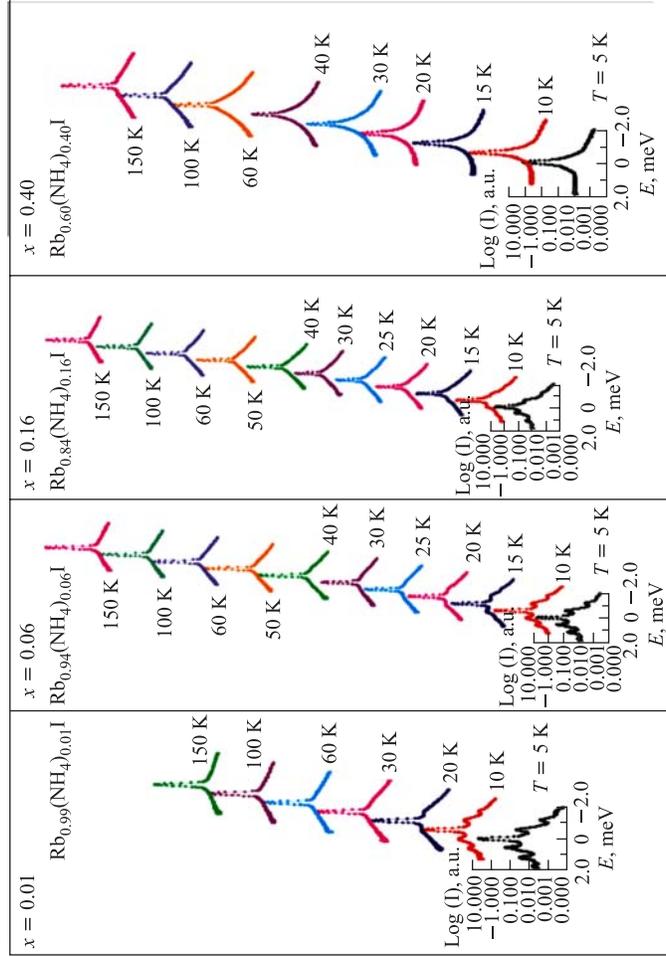


Fig. 5. The intensities of the IINS spectra from  $\text{Rb}_{1-x}(\text{NH}_4)_x\text{I}$  mixed crystals as a function of the temperature and concentration  $x$  (IN6 spectrometer,  $\lambda_0 = 5.12 \text{ \AA}$ , III)

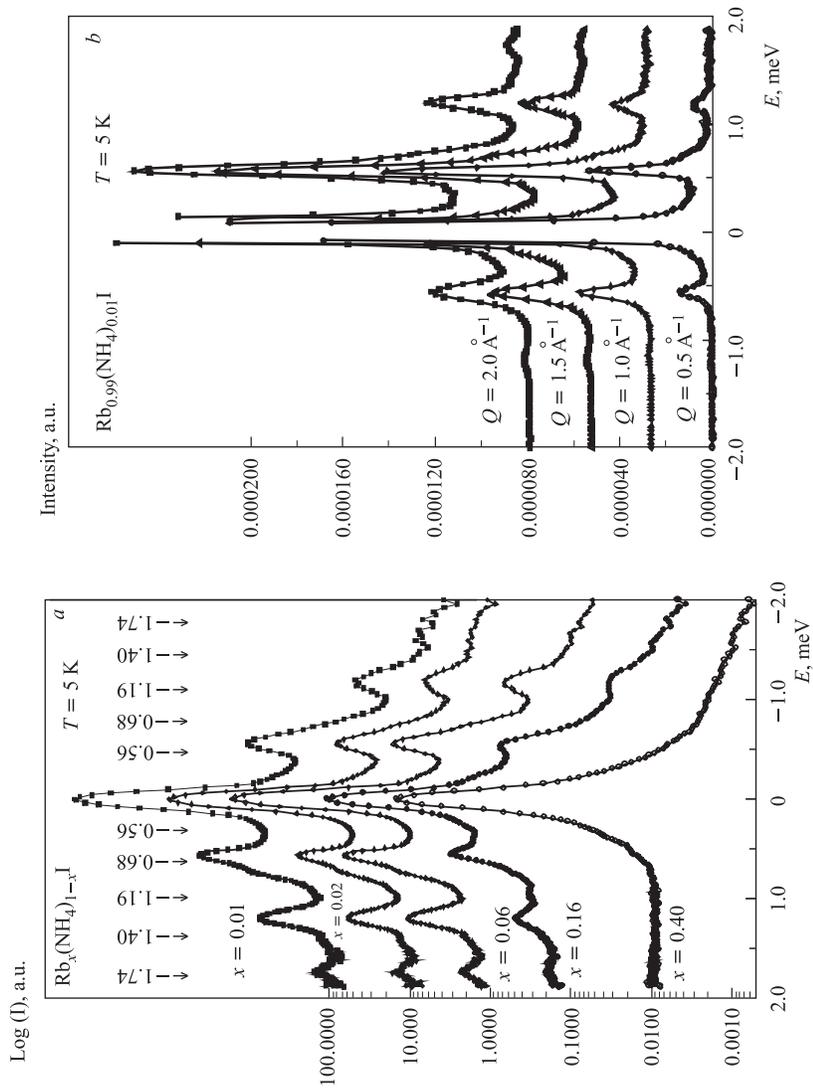


Fig. 6. Tunneling spectra of  $\text{Rb}_{1-x}(\text{NH}_4)_x\text{I}$  mixed crystals: *a*) for different  $x$  at 5 K; *b*) for  $x = 0.01$  at 5 K for different scattering vectors  $Q$  (ILL IN6 spectrometer,  $\lambda_0 = 5.12\text{ \AA}$ )

with energies lower than 2.5 meV were observed at temperature from 5 to 150 K. The IINS spectra for  $x = 0.01, 0.06, 0.16$  and  $0.40$  are presented in Fig. 5.

The observed IINS spectra have two specific peculiarities. The IINS spectra at temperature 5 K for  $x = 0.01, 0.06$  and  $0.16$  are presented by low-energy modes determined by tunneling resonance transitions between splitted energy levels of ground librational level. With the increasing of the temperature from 5 K the intensities of tunneling resonance peaks fall and disappear fully near 20–30 K simultaneously with increasing of quasielastic incoherent scattering contribution. The low-energy tunneling modes from mixed crystal with  $x = 0.40$  are not observed except quasielastic incoherent scattering contribution.

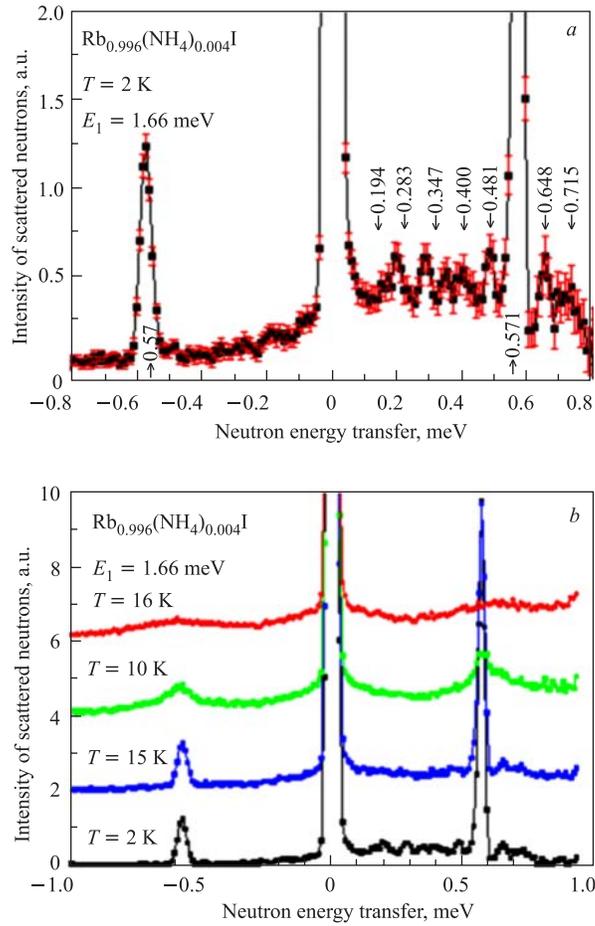


Fig. 7. Tunneling spectra of  $\text{Rb}_{0.996}(\text{NH}_4)_{0.004}\text{I}$  mixed crystal: *a*) at 2 K; *b*) at different temperatures (ILL IN5 spectrometer,  $\lambda_0 = 7.0 \text{ \AA}$ )

Observed low-energy tunneling modes for the  $\text{Rb}_{1-x}(\text{NH}_4)_x\text{I}$  mixed crystals with  $x = 0.01, 0.02, 0.06, 0.16$  and  $0.40$  at temperature  $5\text{ K}$  are presented in Fig. 6, *a*. The intensities of the tunneling modes for sample with  $x = 0.01$  as a function of the scattering vector at  $5\text{ K}$  are presented in Fig. 6, *b*. The energies of selected rotational tunneling modes are presented in the Table.

The low-energy modes of  $\text{Rb}_{1-x}(\text{NH}_4)_x\text{I}$  mixed crystals were observed earlier in  $\text{Rb}_{0.971}(\text{NH}_4)_{0.029}\text{I}$  and some other ammonium–alkali–metal halide lattices in similar energy transfer region [3–5]. This was explained as rotational tunneling modes, due to good agreement with the results of calculations of rotational tunneling modes for  $\text{NH}_4^+$  in  $\text{KBr}$  [10–12].

The measurements of the IINS spectra for  $\text{Rb}_{0.996}(\text{NH}_4)_{0.004}\text{I}$  mixed crystal in the region of energy transfer  $-1.0 < E < 1.0\text{ meV}$  were carried out on the IN5 spectrometer using  $\lambda_0 = 7.0\text{ \AA}$  (resolution  $\Delta E = 25\text{ }\mu\text{eV}$ ) at  $2\text{ K}$ . The observed low-energy modes are presented in Fig. 7, *a*, and the influence of temperature on the IINS intensities from the  $\text{Rb}_{0.996}(\text{NH}_4)_{0.004}\text{I}$  mixed crystal is presented in Fig 7, *b*. The energies of selected low-energy rotational tunneling modes in the energy transfer region  $-1.0 < E < 1.0\text{ meV}$  are presented in the Table.

### 3. DISCUSSION

The Table presents the values of all the measured resonance modes within the energy region from  $0.15$  to  $12\text{ meV}$ . It also gives calculated values of rotational tunneling states for  $\text{NH}_4^+$  molecular ion impurities in  $\text{KBr}$  in the energy region from  $0.53$  to  $7.25\text{ meV}$ . The resonance modes observed in  $\text{Rb}_{1-x}(\text{NH}_4)_x\text{I}$  mixed crystals can be directly identified by comparison with the calculated energies of rotational tunneling modes in  $\text{K}_{1-x}(\text{NH}_4)_x\text{Br}$  mixed crystals [10–12]. However, it is known from [4, 5] that the measured energies for rotational tunneling states of  $\text{Rb}_{1-x}(\text{NH}_4)_x\text{I}$  and  $\text{K}_{1-x}(\text{NH}_4)_x\text{Br}$  mixed crystals are different for similar rotational tunneling states. Therefore, the comparison of measured energies of resonance modes in  $\text{Rb}_{1-x}(\text{NH}_4)_x\text{I}$  for the identification by rotational tunneling energies calculated for  $\text{K}_{1-x}(\text{NH}_4)_x\text{Br}$  mixed crystals can only be approximate.

Ammonium ion molecular defect at low temperature and in  $\text{C}_{3v}$  octahedron high-symmetry environment is known to have splitting of the librational ground state for account of four-proton system which forms three different types of spin functions with symmetries  $A$  ( $I = 2$ ),  $T$  ( $I = 1$ ) and  $E$  ( $I = 0$ ), where  $I$  is the total nuclear spin of the four protons. The calculated energies of the rotational tunneling modes for  $\text{K}_{1-x}(\text{NH}_4)_x\text{Br}$  are presented in the Table [10–12]. The resonance energies  $0.56, 1.20, 1.72\text{--}1.74, 2.25\text{--}2.57\text{ meV}$  for  $\text{Rb}_{1-x}(\text{NH}_4)_x\text{I}$  with  $x = 0.01, 0.02, 0.06, 0.16$ , are close to calculated rotational tunneling mode of  $2.42\text{ meV}$  [10–12].

However, resonance energies measured at  $0.42, 0.67, 0.93, 1.38\text{ meV}$  for the above-mentioned concentrations of the  $\text{Rb}_{1-x}(\text{NH}_4)_x\text{I}$  mixed crystals are absent among the rotational tunneling levels calculated for  $\text{K}_{1-x}(\text{NH}_4)_x\text{Br}$ .

Comparison of tunneling transition energies of  $\text{Rb}_{1-x}(\text{NH}_4)_x\text{I}$  mixed crystals, obtained at 5 K in the present study, with results for  $\text{Rb}_{1-x}(\text{NH}_4)_x\text{I}$  [3] and  $\text{K}_{1-x}(\text{NH}_4)_x\text{Br}$  [10, 12]

Specim.	$\text{Rb}_{1-x}(\text{NH}_4)_x\text{I}$							$\text{K}_{1-x}(\text{NH}_4)_x\text{Br}$ [10–12]		
	0.004	0.01	0.02	0.06	0.16	0.029 [3]	0.36	0.005		
$T$	2 K	5 K						5 K	Exp.	Calcul.
$E$ , meV										
	0.194									
	0.283									
	0.347									
	0.400									
					0.42					
	0.481									
		0.56	0.56	0.56	0.55	0.56		0.53	0.53	
		0.67	0.68	0.67		(0.66)		0.67		
					0.93					
		1.19	1.19	1.19	1.20	1.21		1.20	1.21	
		1.38	1.4		1.37					
		1.74	1.74	1.73	1.72			1.70	1.74	
				2.33	2.25		2.57	2.25	2.42	
								3.11		
									3.63	
									4.84	
								5.3	5.51	
									6.02	
				6.92	6.90				6.72	
									7.25	

The resonance modes with energies of 6.92 and 6.90 meV are selected in the  $G(E)$  spectra of  $\text{Rb}_{1-x}(\text{NH}_4)_x\text{I}$  for  $x = 0.06$  and  $0.16$ , respectively. These energies are between the acoustic and optic bands of  $\text{RbI}$  (between 4.69 and 9.78 meV). Thus, these resonance energies may be considered as energies of local gap modes [13]. On the other hand, the energies of these resonance modes are close to the calculated energy of the  $\text{K}_{0.995}(\text{NH}_4)_{0.005}\text{Br}$  mixed crystal rotational tunneling mode with the value of 6.72 meV.

The identification of mode with energy of 6.90 meV is not ending. Most probably the temperature dependence of IINS intensity from this mode can give the answer on this question in future experimental study but such measurements now did not carry out.

Measured resonance energies within the region of energy transfer from 0.19 to 0.50 meV for  $\text{Rb}_{1-x}(\text{NH}_4)_x\text{I}$  do not appear among the calculated rotational

tunneling levels for the  $\text{K}_{0.995}(\text{NH}_4)_{0.005}\text{Br}$  mixed crystal. Also, rotational tunneling modes with  $E < 0.5$  meV do not appear among the measured rotational tunneling modes for  $\text{K}_{0.995}(\text{NH}_4)_{0.005}\text{Br}$  mixed crystal.

There is other characteristic that can be used to identify rotational tunneling states: the temperature dependence of the IINS spectra. If the IINS intensities for resonance modes, for which energies are described by the calculated rotational tunneling energies, have similar behavior with increasing temperature, then such resonance modes may be rotational tunneling modes. The modes of the  $\text{Rb}_{1-x}(\text{NH}_4)_x\text{I}$  mixed crystals in the region from  $x = 0.01$  to 0.36 and with energies within the diapason from 0.56 to 2.57 meV all have similar behavior with increasing temperature (see Figs. 4 and 5, *b*). The IINS intensities of resonance modes with energies within  $0.5 < E < 2.5$  meV disappear between 20 and 30 K, and at temperatures higher than 30 K the contribution of quasielastic incoherent neutron scattering in the IINS spectra starts to predominate.

The low-energy modes in the region from 0.19 to 0.48 meV do not correspond to rotational tunneling modes calculated for  $\text{NH}_4^+$  in KBr. Indeed, ammonium ions in the  $\text{Rb}_{1-x}(\text{NH}_4)_x\text{I}$  mixed crystals shifting to off-centre positions can create some dipole moment as, for example, in  $\text{K}_{1-x}(\text{NH}_4)_x\text{I}$  mixed crystals, in which ammonium ions have a dipole moment of 1.4 D due to its off-centre positions [14].

The ammonium ions in the  $\alpha$ -phase of  $\text{Rb}_{1-x}(\text{NH}_4)_x\text{I}$  correspond to  $\text{C}_{3v}$  fundamental orientations in which one of the four N–H bonds lies along the 8 different  $\langle 111 \rangle$ -type orientations. The dipoles of the ammonium ions can tunnel between neighboring orientations and these tunneling transitions can account for resonance scattering of phonons [15, 16].

It is worth notice that low-energy modes were not observed experimentally in the IINS study of  $\text{K}_{0.995}(\text{NH}_4)_{0.005}\text{Br}$  mixed crystal using the ILL IN5 spectrometer with  $\lambda_0 = 6.5$  Å at 1.8 K within the energy region between the elastic peak and the rotational tunneling peak with energy 0.53 meV [12]. However, under similar experimental conditions low-energy peaks are observed in the  $\text{Rb}_{0.996}(\text{NH}_4)_{0.004}\text{I}$  mixed crystal ( $\lambda_0 = 7.0$  Å,  $T = 2$  K). Thus these low-energy peaks seem to be due to reorientational tunneling transitions of dipole moments of ammonium ions [16].

It is interesting to present for the more full understanding of obtained experimental results short discussion of the theory which can help to model the observed peculiarities in  $\text{Rb}_{1-x}(\text{NH}_4)_x\text{I}$  mixed crystals. In the first instance we must consider  $\text{Rb}_{1-x}(\text{NH}_4)_x\text{I}$  as complex system consisting from translational and orientational degrees of freedom. The ammonium molecular ions have owned molecular-like modes and being as molecular impurity can destroy phonon spectrum of clear RbI.

In the case of the  $\text{Rb}_{1-x}(\text{NH}_4)_x\text{I}$  mixed crystals the energy of librational mode of ammonium impurity ion is located higher than maximum energy of

the crystal-host phonon spectrum on the boundary of Brillouin zone. Thus observed low-energy modes can be linked with rotation tunneling modes from splitted levels of ground libration mode of ammonium ion. In order to prove, that observed low-energy modes are resonance modes, the measured IINS spectra from mixed crystals for some ammonium concentrations are presented. The IINS spectra for the  $\text{Rb}_{0.99}(\text{NH}_4)_{0.01}\text{I}$  mixed crystal measured at  $T = 5$  K are presented in Fig. 6, *a* for the momentum transfers with  $Q = 0.5, 1.0, 1.5$  and  $2.0 \text{ \AA}^{-1}$ . Visually the positions of peaks as a function of momentum transfers do not change on the energy scale. Similar measured resonance mode with low energy transfer  $E = 2.57$  meV at  $T = 5$  K from the  $\text{Rb}_{0.64}(\text{NH}_4)_{0.36}\text{I}$  mixed crystal is invariant as a function of momentum transfers with  $Q = 0.5, 1.0, 1.5, 2.0$  and  $2.5 \text{ \AA}^{-1}$ . The obtained experimental data point out that observed resonance modes do not have the dispersion.

## CONCLUSION

The investigation of the dynamics of the  $\text{Rb}_{1-x}(\text{NH}_4)_x\text{I}$  mixed crystals was carried by means of inelastic incoherent neutron scattering (IINS) from powder samples. In this case the measurements of the intensity of IINS spectra are carried out as a function of energy transfer including the integration over all momentum transfer from phonon wave vectors. Such measurements from the  $\text{Rb}_{1-x}(\text{NH}_4)_x\text{I}$  mixed crystals led to the observation of resonance modes suited to rotational tunneling transitions between splitted levels of ground librational level of ammonium ion, to resonance modes of multiple moments (dipole moment, quadrupole, etc. moments) of ammonium ions or to local gap modes of ammonium ions. The observation of resonance modes points on small damping between resonance modes of ammonium ions and phonon modes of crystal-host.

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