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AMMONIUM DYNAMICS IN THE DISORDERED α-PHASE OF $K_{1-x}(NH_4)_xY$ (Y = Cl, Br, I). A NEUTRON SCATTERING STUDY

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Introduction

Ammonium salts exhibit rich structural polymorphism induced by the different ordering of NH_4 groups in crystalline lattices [1]. Anharmonic effects due to fast reorientation of ammonium ions make it difficult to study lattice dynamics of disordered, and even of ordered phases, above ca. 100 K. Solid solutions of ammonium and potassium halides form different solid phases of ammonium halides depending on the ammonium concentration which are possible to be frozen to liquid helium temperatures. This permits studies of the harmonic dynamics of disordered crystals, ordering effects and of quantum mechanic effects on the excitations of NH_4 groups.

Ammonium halides demonstrate a series of structural phase transitions: α-β-δ in NH_4Cl, α-β-γ-δ in NH_4Br and α-β-γ in NH_4I [1]. The α- and β-phases have a cubic crystal structure of the NaCl and CsCl type, respectively, with disordered ammonium ions. In the α-phase the NH_4 tetrahedron is octahedrally coordinated by the surrounding halogen ions. It is generally believed that NH_4 ions adopt the C_{3v} symmetry of the site, where three of the hydrogen atoms are directed toward the halogen anions, while the fourth points towards one of the face centre of the octahedron. The cubic symmetry of this phase is stabilised by fast reorientations of the NH_4 group among eight symmetry equivalent positions. In the β-phase the NH_4 groups reorient between two energetically equivalent orientations within a cube constituted by the surrounding halogen anions [2]. Transitions from disordered to ordered phases are determined by competitions of direct octopole-octopole interactions of ammonium ions and indirect interactions of halide ions via polarisation. The direct interaction favours the ferroelectric state, while the indirect one tends to the antiferroelectric state of ammonium orientations in the ordered phases [3]. The existence of the dipole moment $\mu = 1.4$ D for ammonium ions in the α-phase of the $K_{1-x}(NH_4)_xI$ mixed crystals was detected by dielectric spectroscopy [4].

Presently, $K_{1-x}(NH_4)_xI$ mixed salts attract increasing interest because of their low-temperature orientational glass (OG) phase. At low temperatures and $0.3<x<x_c$, the OG phase with an antiferroelectric short range order of NH_4 ions has a cubic structure of the α-phase of the NaCl type. Above the critical ammonium concentration x_c, estimated between $x = 0.72$ and 0.82, there occurs a phase transition from NaCl- to CsCl-type structure [5]. More recent dielectric and structural studies [6,7] of the x-T phase diagram of $K_{1-x}(NH_4)_xI$ indicate the presence of different OG phases of g_1, g_2 and g_3 in the concentration range $0.17<x<0.55$ and of the ε-, β- and γ-phases in the concentration region $0.55<x<1.0$.

The α-phase of potassium halides doped with ammonium of low concentration was used to study the rotation tunnelling of NH_4 ions [8-11]. These investigations have shown that the tunnelling transitions of ammonium ions can be satisfactorily described by the single ion approximation [8]. With increasing ammonium concentration the collective behaviour starts to arise due to an increasing role of the ammonium-ammonium interaction [9,10]. It is suggested that the tunnelling excitations are suppressed by the formation of the glass phase in $K_{1-x}(NH_4)_xI$ mixed crystals [9]. The temperature study shows a continuous transition from quantum ($T < 5$ K) to classical mode ($T > 20$ K) of reorientational motion [8,9]. A model of rotational tunnelling states in the energy range up to 8 meV has been proposed for the doped NH_4 ions in a KBr crystal [11].

An IINS study of the dipolar glass $K_{1-x}(NH_4)_xI$ at 20K in the concentration range $0.05<x<0.7$ has demonstrated the existence of three distinct inelastic features at ca. 10, 21 and 31 meV [12]. Our neutron scattering investigations of $K_{1-x}(NH_4)_xI$ mixed salts show an additional band at ca. 2.5 meV [13,14].

In this paper we present the results obtained for the α-phase of $K_{0.95}(NH_4)_{0.05}Br$ and $K_{0.95}(NH_4)_{0.05}Cl$ mixed salts together with the results of our study of the NH_4 concentration effect on ammonium dynamics in $K_{1-x}(NH_4)_xI$ mixed salts and on the disorder-to-order phase transition at 10 K.

Experimental results

The investigated potassium-ammonium mixed crystals were prepared by the evaporation of corresponding stoichiometric aqueous solutions under a pressure of ca. 10 Pa at room temperature. The powdered samples were dried for a few hours at 50°C at ambient pressure before the neutron scattering experiment. Neutron powder diffraction (NPD) and inelastic incoherent neutron scattering (IINS) spectra were measured simultaneously by the time-of-flight method with the high-resolution spectrometer NERA [15] at the IBR-2 pulsed reactor. NPD spectra were measured at four scattering angles: 45°, 69°, 135° and 144°, and IINS spectra were measured at fifteen scattering angles from 20° to 160°. The energy of the incoming neutrons was time-of-flight analysed on a 109 m flight path from reactor core to sample. In the case of inelastic scattering, the energy of the scattered neutrons was fixed by a beryllium filter and pyrolitic graphite analysers.

The NPD spectra allow us to check the phase of the investigated samples and study the concentration and temperature dependence of lattice parameters. As an example, the NPD spectra of $K_{1-x}(NH_4)_xI$ at 10 K measured at the scattering angle 135° are presented in Fig. 1. Strong reflections from the aluminium walls of the cryostat at lattice distances between d = 2.33 and 2.02 Å, were cut off. The structural phase transition from disorder α- to ordered γ-phase is clearly seen in the NPD spectra. The lattice parameters and the volume per formula unit calculated from these NPD spectra are presented in Fig.2.

A comparison of IINS spectra (summed over 15 scattering angles) of $K_{0.95}(NH_4)_{0.05}Br$ mixed salt obtained at 290, 80 and 10 K with IINS spectrum of KBr at 80 K presented in Fig. 3, allows us to conclude about ammonium excitations in the disordered α-phase. The IINS spectrum measured at 290 K versus the wavelength of incoming neutrons testifies to a wide energy distribution of ammonium excitations in the range from ca. 1 Å to the position of the elastic peak at 4.15 Å. The quasielastic neutron scattering (QNS) wings observed around the elastic peak, which indicate a fast stochastic reorientation of NH_4 groups, narrow with decreasing temperature. The spectrum at 80 K, shows the peaks corresponding to the librational and translational excitations of ammonium (at neutron wavelength of ca. 1.45 and 1.65 Å, respectively) above the band of lattice vibration of KBr crystal, whose cut-off energy corresponds to the incoming neutrons wavelength of ca. 2 Å. In the range of KBr lattice vibrations, the IINS spectrum of $K_{0.95}(NH_4)_{0.05}Br$ mixed crystal at 10 K shows two additional excitations at ca. 2.4 and 3.5 Å.

The amplitude weighted phonon densities of state G(ω) calculated from these IINS spectra in the one-phonon incoherent scattering approximation [15,16] are presented in Fig. 4. Four distinct bands, which correspond to excitations of ammonium ions in the disorder α-phase of $K_{0.95}(NH_4)_{0.05}Br$, are clearly observed at 10 K. Two of them located inside the phonon spectrum of KBr are usually called the resonant modes. These modes at about 20 and 80 cm^{-1} are related to rotational tunnelling excitations [8,10] and librations of ammonium ions around the dipolar axis [12], respectively. The modes localised at about 200 and 300 cm^{-1}, correspond to translational and librational vibrations (perpendicular to the dipolar axis) of ammonium ions, respectively. These two modes were observed for the ordered phase of NH_4Br at ca. 161 and 343 cm^{-1}, respectively [17].

The temperature dependence of the amplitude weighted phonon density of states G(ω) for a $K_{0.95}(NH_4)_{0.05}Cl$ mixed crystal is presented in Fig. 5. The lattice vibrations of KCl are quite intense in the G(ω) spectrum of $K_{0.95}(NH_4)_{0.05}Cl$ because of a relatively high scattering cross-section of chlorine atoms. The low frequency resonant mode of ammonium at ca. 20 cm^{-1} is strong at 10 K. The second resonant mode is lost in a high background of potassium chloride lattice vibrations and should be seen at a higher ammonium concentration. The localised tranlational and librational modes are well expressed at ca. 230 and 340 cm^{-1}. The energies of the corresponding modes in the ordered phase of NH_4Cl were observed at ca. 180 and 395 cm^{-1}, respectively [15].

We have investigated ammonium-potassium iodide in a wide range of concentrations ($0.0<x<1.0$) and temperatures (10-290 K) [13,14]. The results of our IINS studies of $K_{1-x}(NH_4)_xI$ solid solutions at 10 K are presented in Fig. 6. The G(ω) spectra for the disorder α-phase within an entire concentration range of $0.05<x<0.60$ show four distinct ammonium excitations at ca. 20, 70, 175 and 250 cm^{-1}. The bandwidth of these excitations is broader than the resolution function of the spectrometer. The G(ω) spectra of the γ-phase only display localised ammonium excitations. The bands at ca. 150 and 300 cm^{-1} marked as ν_5 and ν_6 correspond to translational and librational phonon excitations of NH_4 groups in the crystal, respectively. The IINS spectra of the ordered phases of ammonium halides measured at low temperatures also display higher energy bands corresponding to the $\nu_5+\nu_6$ combination band and $2\nu_6$ overtone excitations. They are very weak in the G(ω) spectra of the disorder α-phase. The ν_6 mode is the most intense band in the G(ω) spectra of the γ-phase and its width is close to the resolution of the NERA spectrometer. This mode becomes much broader and weaker in the α-phase and its energy changes from ca. 300 to ca. 250 cm^{-1}, which corresponds to a jump-like increase in the volume per formula unit at order-disorder phase transition. The average energy of translational phonons for the disorder α-phase slightly decreases as the lattice expands due to increasing ammonium concentration (see Fig. 2.). The G(ω) for these excitations is not disturbed much by the α- to γ-phase transition.

The excitation at ca.70 cm^{-1} is interpreted as corresponding to librations of ammonium ions around the dipolar axis if it is assumed that tetrahedral ammonium ions adopt the C_{3v} symmetry site in an octahedral halogen cage [12]. The energy of this excitation slightly increases with increasing concentration of ammonium in mixed salts in spite of lattice expansion.

It seems that the broad resonant mode at ca. 20 cm^{-1} observed in our investigations of mixed potassium-ammonium halides corresponds to tunnelling transitions of ammonium tetrahedron in an octahedral field of halogen ions. At low concentrations ($x<0.01$) and temperatures ($T<5K$) these transitions are observed as sharp lines in IINS spectra [8-11]. With increasing concentration and temperature these excitations broaden and spread out. In our case ($T=10$ K and $0.05<x<0.6$), low energy excitations convolute with the NERA spectrometer resolution function [15] which is similar to the gaussian with FWHM at ca. 5 cm^{-1} if the energy transfer is ca. 20 cm^{-1}. The "tunnelling transitions" in these conditions are observed as a broad band at ca. 20 cm^{-1} whose maximum and width slightly increase with ammonium concentration. Our recent temperature study of the sample $K_{0.65}(NH_4)_{0.45}I$ shows that the width of the band at ca. 20 cm^{-1} increases with temperature and at about 30 - 40 K this band disappears transforming into wide quasielastic wings [18].

Discussion and conclusions

The amplitude weighted phonon density of states $G(\omega)$ of ammonium in the NaCl type structure of potassium-ammonium halides was obtained over the entire energy range of lattice vibrations of the α-phase. Ammonium dynamics in this phase is characterised by four distinct bands whose average energies are shown in Fig. 7 as a function of the nitrogen-halogen distance. The average energies of translational (ν_5) and librational (ν_6) ammonium excitations in a low temperature ordered phases of the CsCl type structure of ammonium halides are also marked for the sake of comparison in Fig. 7. The transition from NaCl to CsCl type structure is related to an increase of the nitrogen-halogen distance (in the cubic structure from $a/2$ to $\sqrt{3}a/2$, where a is the halogen-halogen distance). This means that the (ν_5) translational modes have higher energies in the α-phase than in the ordered phases of ammonium halides. The (ν_6) librational modes of ammonium ions are more affected by the geometry and number of the surrounding halogen atoms that change from six in the octahedral symmetry in the α-phase to eight in the cubic or tetragonal symmetry in the ordered phases. The energies of librational modes in the ordered phases of ammonium halides are higher than in the α-phase despite of larger nitrogen-halogen distances.

The existence of two additional bands at lower energies of ammonium excitations in the α-phase can be explained in terms of the so called "triple approach" model, where tetrahedral ammonium ions adopt the C_{3v} symmetry in the octahedral surrounding of halogen ions. Three rotational degrees of freedom of the ammonium tetrahedron having a triple degenerated F_1 character in the O_h symmetry site of the cubic cell split into two modes of the E and A_2 character, respectively, in the C_{3v} symmetry site. The double degenerated mode ν_E relates ammonium librations around the axes perpendicular to the dipole moment along the C_{3v} symmetry axis [12]. A low energy of the ν_A mode implies very low potential barriers for ammonium librations around the C_{v3} symmetry axis and strong splitting of the tunnelling states [11]. Tunnelling spectra are very sensitive to the ammonium concentration and the lines below ca. 10 cm^{-1} collapse completely into a quasi-elastic line at $x = 0.28$ [9]. The concentration dependencies of higher frequency tunnelling transitions have not been investigated yet. A low energy

band at ca. 20 cm^{-1} was observed in our spectra of the α-phase of $K_{1-x}(NH_4)_xI$ mixed salts over the whole concentration range $0.05<x<0.60$.

The concentration dependencies of the average energies of ammonium excitations in $K_{1-x}(NH_4)_xI$ mixed salts are presented in Fig. 8. According to recent knowledge about the x-T phase diagram of $K_{1-x}(NH_4)_xI$ solid solutions, our samples of ammonium-potassium iodide mixed salts at $x = 0.6$ and 0.8, should correspond to the ε and β phases, respectively. The existence of a transition from NaCl type structure of the ε-phase [5] to CsCl type structure of the β-phase is confirmed by our NPD and IINS spectra (see Figs. 1,2 and 6). An essential difference in ammonium dynamics is only observed for these two different types of crystal lattices. The G(ω) of the α-phase at 10 K looks quite similar over the whole concentration range $0.05<x<0.6$. The local distortions which break the *fcc* symmetry in glassy phases and a complex dipolar order of the ε-phase seem to be less important than the simple concentration dependence of the average energies of ammonium excitations. Therefore, it would be reasonable to approximate the average energies of these excitations to a hypothetical α-phase of ammonium iodide at low temperature. It would be interesting to calculate the lattice dynamics of the α-phase with antiferroelectric ordering of ammonium ions or of the ε-phase with complex dipolar ordering and compare them with the experimental G(ω) spectra presented in this paper. The lattice dynamics calculations of the ordered phase of ammonium chloride in a rigid molecule model [19] explain satisfactorily the experimental dispersion curves of ND_4Cl and the G(ω) spectra of NH_4Cl. The lattice dynamics model used in the study of the dispersion curves of ND_4I in the α-phase at 296 K [20] could only explain the translational band in the G(ω) spectra presented in Fig. 6.

The dipolar glass interactions similar to those in spin glasses are not expected to change excitation energies but may influence their bandwidths [12]. The bandwidths of the four distinct ammonium excitations in the α-phase of ammonium-potassium halides are larger than the resolution function and they slightly increase with ammonium concentration for low energy resonant modes and for the translational mode but decreases for the ν_E librational mode. It is difficult, however, to analyse them qualitatively because we measure the density of states but not the width of a particular excitation at well defined energy and momentum transfers. The concentration dependencies of the average energies of ammonium excitations in the α-phase of the $K_{1-x}(NH_4)_xI$ solid solutions can be seen in Fig. 8. The average energies of low frequency resonant modes increase with ammonium concentration in contrast to lattice expansion. It means that the direct ammonium-ammonium interaction affects the potential barrier hindering the rotations about the C_{3v} dipolar axis.

Acknowledgements

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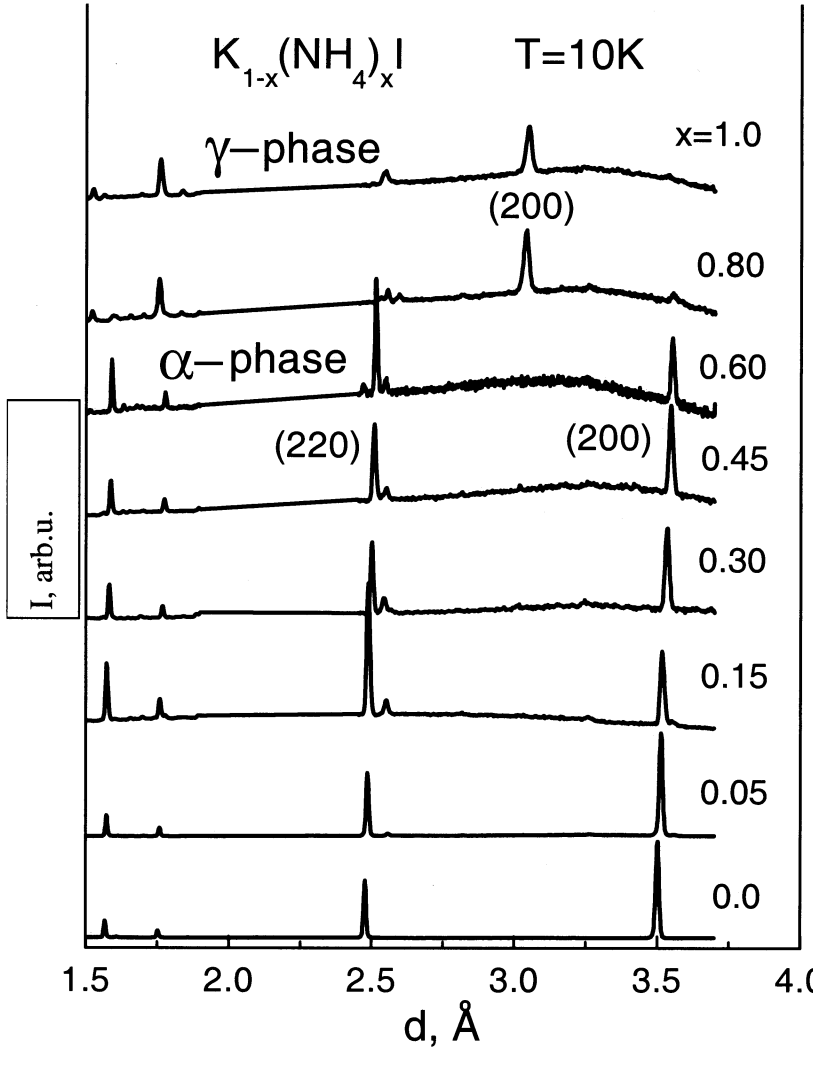

Fig. 1. The neutron powder diffraction spectra of ammonium-potassium iodide at 10K.

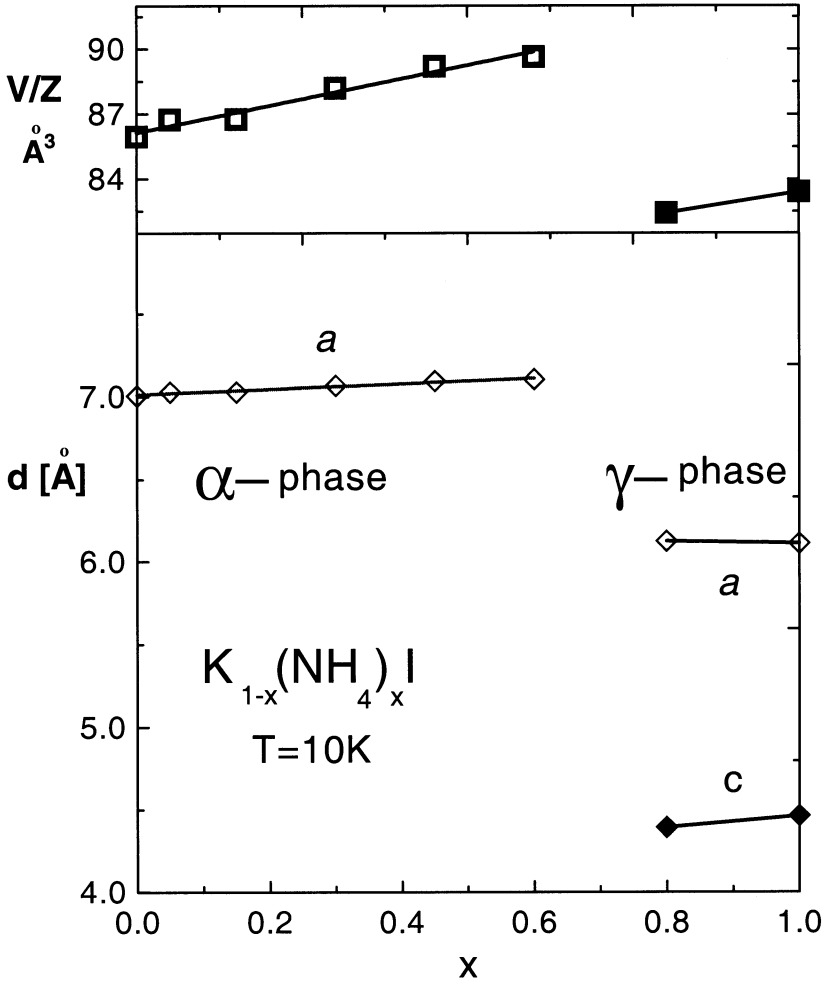

Fig. 2. The lattice parameters and volume per formula units of $K_{1-x}(NH_4)_xI$ mixed salts at 10 K versus ammonium concentration.

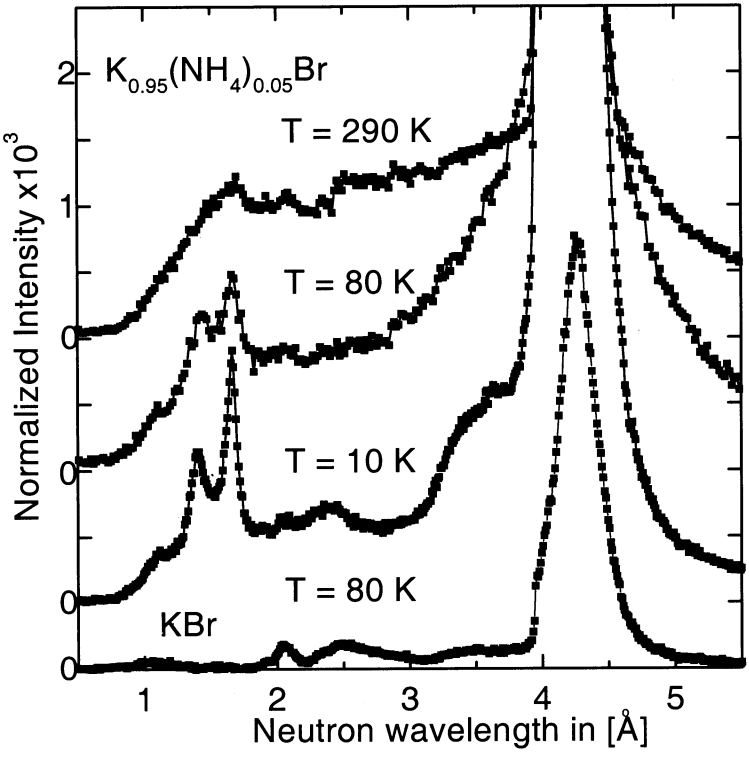

Fig. 3. The temperature dependence of the IINS spectra of KBr and $K_{0.95}(NH_4)_{0.05}Br$ crystals.

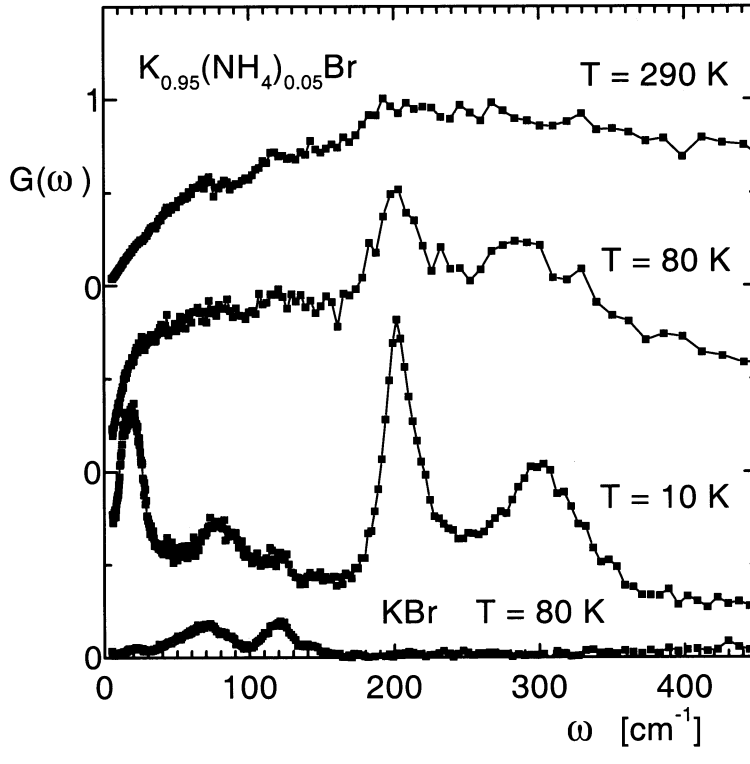

Fig. 4. The amplitude weighted phonon density of states G(ω) for potassium bromide at 80 K and $K_{0.95}(NH_4)_{0.05}Br$ mixed crystal at different temperatures.

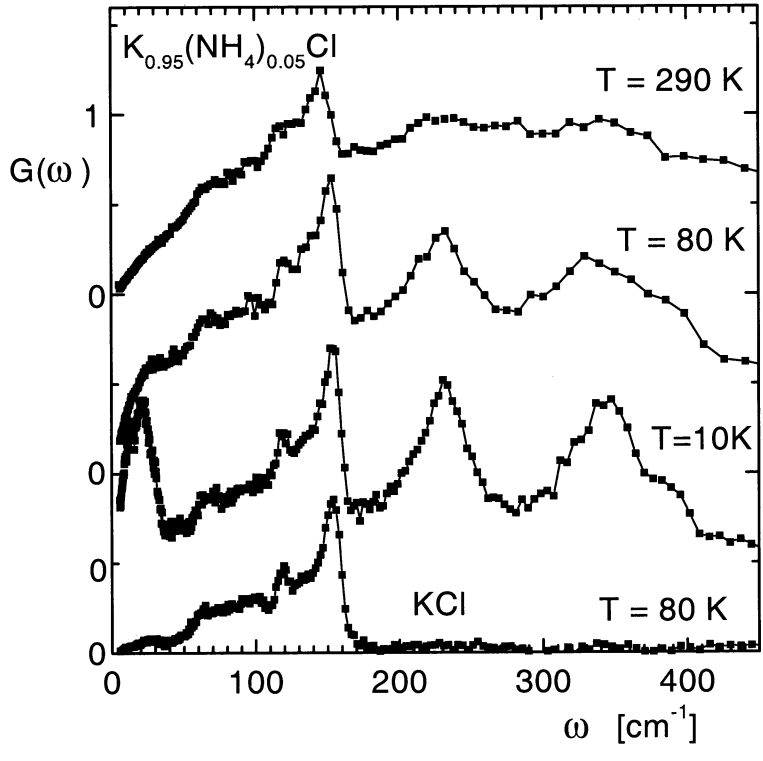

Fig. 5. The amplitude weighted phonon density of states G(ω) for potassium chloride at 80 K and $K_{0.95}(NH_4)_{0.05}Cl$ mixed crystal at different temperatures.

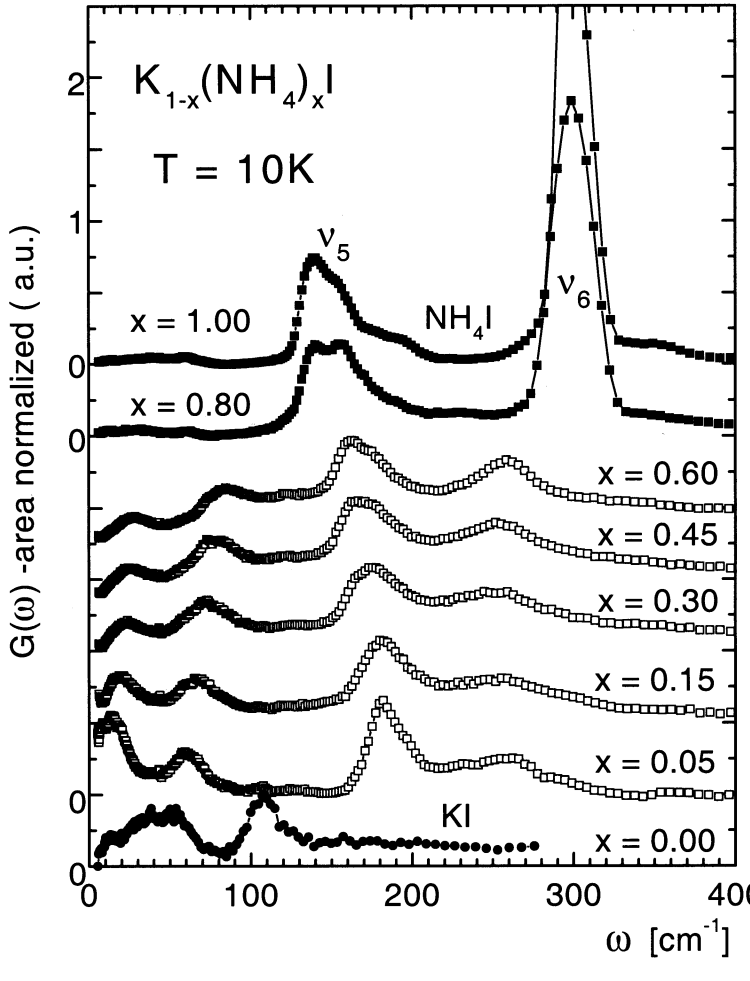

Fig. 6. The concentration dependence of the amplitude weighted phonon density of states G(ω) of KI at 80 K (solid circles) and $K_{1-x}(NH_4)_xI$ mixed salts at 10K, for the α-phase (open squares) and γ-phase (solid squares).

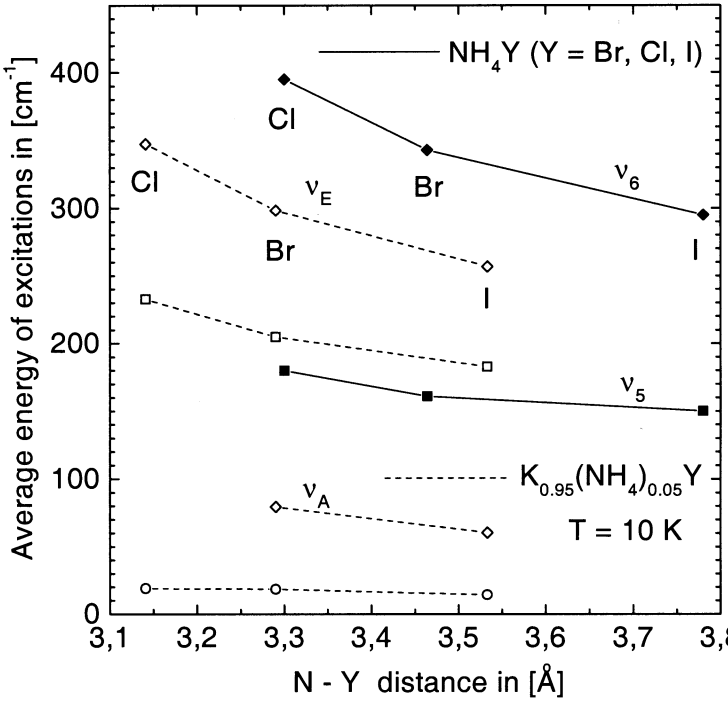

Fig. 7. The comparison of the average energies of ammonium excitations: in the disorder α-phase of $K_{0.95}(NH_4)_{0.05}Y$ (Y = Br, Cl, I) mixed salts at 10 K (dashed lines and open symbols), and the ordered phases of ammonium halides at low temperatures (solid lines and symbols).

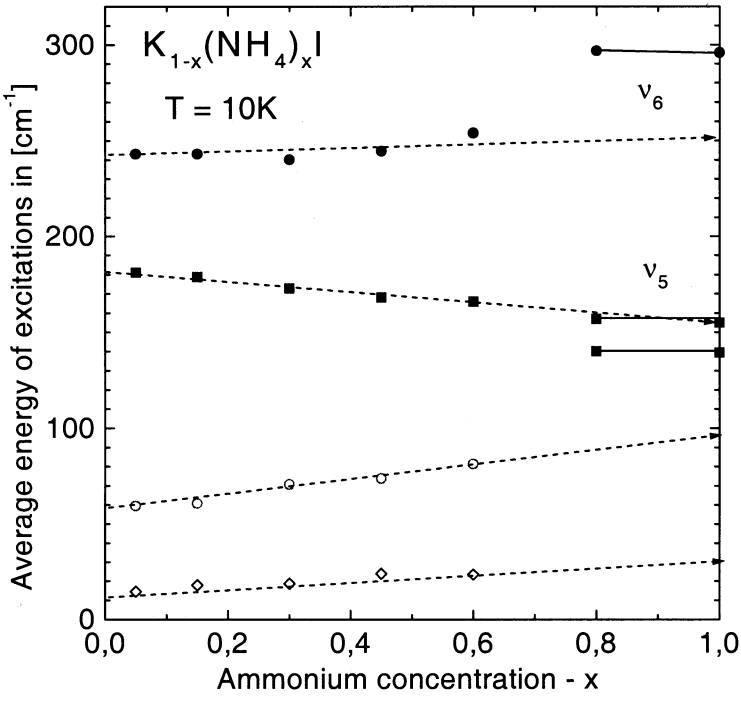

Fig. 8. The concentration dependencies of the average energies of ammonium excitations in the α (dashed lines) and γ (solid lines) phases of $K_{1-x}(NH_4)_xI$ mixed salts at 10 K.

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18. Natkaniec, I., L.S.Smirnov and A.I.Solov'ev. (1997). Isledovanie dinamiki ammonia v smieshannykh kristallakh $K_{1-x}(NH_4)_xHal$ (Hal = Cl, Br, I) medodom nieuprugovo rasseyania neytronov. In *Proc. National Conference on Materials Investigation by X-ray, SR, Neutrons and Electrons, Dubna 1997, JINR Report*, Vol. III, pp. 25-30.
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Динамика аммония в разупорядоченной α-фазе
$K_{1-x}(NH_4)_xY$ (Y = Cl, Br, I).
Исследование с помощью рассеяния нейтронов

С помощью нейтронной порошковой дифракции и неупругого некогерентного рассеяния нейтронов исследовано влияние температуры и концентрации на параметры решетки и амплитудно-взвешенную плотность фононных состояний в смешанных солях аммониево-калиевых галогенидов. В разупорядоченной α-фазе (типа NaCl) ионы аммония совершают быструю стохастическую переориентацию со скоростями фононных частот до температуры 80 K. При 10 K спектры неупругого некогерентного рассеяния нейтронов проявляют четыре различные моды возбуждения аммония: две резонансные — ниже и две локализованные — выше энергии обрезания Дебая галогенидов калия. Высокоэнергетические локализованные моды соответствуют трансляционным и либрационным колебаниям ионов NH_4. Эти моды типичны для упорядоченных фаз галогенидов аммония. Изучается влияние концентрации аммония на локализованные и резонансные моды для смешанных солей $K_{1-x}(NH_4)_xI$. Гармонические возбуждения аммония в гипотетической низкотемпературной α-фазе NH_4I аппроксимируются при 30, 95, 155 и 250 $см^{-1}$. В реальной низкотемпературной упорядоченной γ-фазе NH_4I наблюдаются аммониевые трансляционные колебания при 140–160 $см^{-1}$ и либрационные колебания при 300 $см^{-1}$.

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

Препринт Объединенного института ядерных исследований. Дубна, 2002

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Ammonium Dynamics in the Disordered α-Phase
of $K_{1-x}(NH_4)_xY$ (Y = Cl, Br, I). A Neutron Scattering Study

The effect of temperature and concentration on the lattice parameters and amplitude-weighted phonon density of states in mixed salts of ammonium-potassium halides is investigated by neutron powder diffraction and incoherent inelastic neutron scattering. In the disordered α-phase (NaCl type) ammonium ions exhibit a fast stochastic reorientation at phonon frequency rates down to ca. 80 K. At 10 K, the incoherent inelastic neutron scattering spectra display four distinct ammonium excitations: two (resonant) modes below and two (localized) above the Debye cut-off energy of potassium halides. High-frequency localized modes correspond to translational and librational vibrations of NH_4 ions. These modes are typical for the ordered phases of ammonium halides. The effect of ammonium concentration on localized and resonant modes is studied for the $K_{1-x}(NH_4)_xI$ mixed salts. The harmonic excitations of ammonium in a hypothetical low-temperature α-phase of NH_4I are approximated to ca. 30, 95, 155 and 250 cm^{-1}. In a real low-temperature ordered γ-phase of NH_4I, translational ammonium vibrations are observed at ca. 140–160 cm^{-1} and librational vibrations at ca. 300 cm^{-1}.

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

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