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THE INVESTIGATION OF AMMONIUM ION DYNAMICS IN $K_{1-x}(NH_4)_xBr$ MIXED CRYSTALS:
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The x-T phase diagram of the $K_{1-x}(NH_4)_xBr$ mixed crystals and ammonium ion dynamics are studied by neutron powder diffraction and inelastic incoherent neutron scattering in ammonium concentration region $0.05 \leq x \leq 1.0$ and temperature interval from 22 to 290 K. The cross section of x-T phase diagram at 22 K shows that cubic disordered α-phase is observed for x=0.05, 0.14 and 0.24, two-phase region of α-phase and β-phase co-existence is observed at x=0.52 and 0.83. The low energy resonance modes with E_r^1=2.1-4.2 meV and E_r^2=8.8-12.5 meV and localized translational ν_5 mode with energy E=23-25 meV and librational ν_6 mode with energy E=35.4-37.7 meV are observed in α-phase, only ν_5 mode with energy 18 meV and splitted ν_6 mode with energies 40.7 and 43.4 meV are observed in β-phase. Splitted ν_6 mode is observed in NH_4Br in δ-phase at 22 K, in γ-phase at 123 K but at 220 K the splitting of ν_6 mode is not observed due to the anharmonicity as and in β-phase at 250 K and above.

ИССЛЕДОВАНИЕ ДИНАМИКИ ИОНОВ АММОНИЯ В СМЕШАННЫХ КРИСТАЛЛАХ $K_{1-X}(NH_4)_XBR$.

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x-T фазовая диаграмма смешанных кристаллов $K_{1-x}(NH_4)_xBr$ и динамика ионов аммония исследованы с помощью нейтронной порошковой дифракции и неупругого некогерентного рассеяния нейтронов в области концентрации аммония $0.05 \leq x \leq 1.0$ и интервала температуры от 22 до 290 K. Сечение x-T фазовой диаграммы при 22 K показывает, что кубическая разупорядоченная α-фаза наблюдается при x=0.05, 0.14 и 0.24, двух-фазная область сосуществования α- и β-фаз наблюдается для x=0.52 и 0.83. Резонансные моды низкой энергии с E_r^1=2.1-4.2 meV и E_r^2=8.8-12.5 meV и локальные трансляционная мода ν_5 с энергией E=23-25 meV и либрационная мода ν_6 с энергией E=35.4-37.7 meV наблюдаются в α-фазе, только мода ν_5 с энергией 18 meV и оасщепленная мода ν_6 с энергиями 40.7 и 43.4 meV наблюдаются в β-фазе. Расщепленная мода ν_6 наблюдается в NH_4Br в δ-фазе при 22 K, и в γ-фазе при 123 K но при 220 K расщепленная мода ν_6 не наблюдается, что обусловлено ангармонизмом как и в β-фазе при250 K так и выше.

Fig. - 12, Ref. – 7.

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Introduction

The crystal structures of KBr and NH_4Br have different space groups at room temperature and form the $K_{1-x}(NH_4)_xBr$ solid solutions with limited region near K and NH_4^+ [1]. KBr do not have phase transitions from high temperature to low but NH_4Br undergoes the series of phase transitions [2,3]:

α-phase ⇔ 410.8K ⇔ β-phase ⇔234.9K ⇔ γ-phase ⇔ (105-78) K ⇔ δ-phase.

The cubic disordered α-phase has space group Fm3m-O_h^5, the cubic disordered β-phase has space group Pm3m-O_h^1, the ordered tetragonal γ-phase – space group P4/nmm-D_{4h}^7 and ordered cubic δ-phase – space group P-43m – T_d^1. It is worth to note that until recent time the x-T phase diagram of the $K_{1-x}(NH_4)_xBr$ mixed crystals was studied seldom. So it is known that the $K_{1-x}(NH_4)_xBr$ mixed crystals are cubic disordered α-phase up to low temperatures in the region of small ammonium concentrations.

Earlier $K_{1-x}(NH_4)_xBr$ were studied in region $x \leq 0.05$ by the neutron tunneling and inelastic incoherent neutron scattering as well. The low energy resonance mode with E_r^1=2.3 meV was observed in $K_{0.95}(NH_4)_{0.05}Br$ mixed crystal at 10 K in [4], however other low energy mode with possible energy E_r^2=~7-10 meV which was observed in $K_{0.95}(NH_4)_{0.05}I$ [4] could not be separated correctly from translational optic mode.

The results of the ammonium dynamics study of the $K_{1-x}(NH_4)_xBr$ solid solution in the wide ammonium concentration region at T=20 K are presented here. Resent measurements show that disordered α-phase is observed up to x=0.24 and the low energy modes with energies 2.3-3.4 and 8.3-10.5 meV are observed in this region. The librational mode ν_6 is observed in β-phase as splitted on two sub-bands.

Experiment and results

There are presented the results of the study of the x-T phase diagram of the $K_{1-x}(NH_4)_xBr$ mixed crystals and ammonium dynamics in different phases observed at low temperature. These investigations were carried out by the neutron powder diffraction (NPD) and the inelastic incoherent neutron scattering (IINS) on the samples of the $K_{1-x}(NH_4)_xBr$ with ammonium concentrations x=0.0, 0.05, 0.14, 0.24, 0.52, 0.83 and 1.0 at low temperature T=23 K. These powder samples of the $K_{1-x}(NH_4)_xBr$ mixed crystals were prepared from appropriate water solutions by slow evaporation. The neutron scattering spectra of NPD and IINS were measured on the NERA-PR neutron spectrometer set on IBR-2 (FLNP JINR, Dubna, Russia). This spectrometer gives the possibility to obtain NPD and IINS spectra from a sample simultaneously. The generalized phonon densities of states G(E) were calculated from the IINS spectra in one-phonon incoherent approximation [5,6].

Ammonium concentrations x of the $K_{1-x}(NH_4)_xBr$ mixed crystals were determined by the measure of intensities of neutron scattering from hydrogen translational ν_5 and librational ν_6 modes of these samples using their IINS spectra normalized on weights and measuring times.

The obtained NPD spectra from the $K_{1-x}(NH_4)_xBr$ mixed crystals for x=0.14, 0.24, 0.52 and 0.83 at the T=23 K are presented in Fig. 1 and from NH_4Br at different temperatures in Fig. 2. The NPD spectra show that samples with x=0.14 and 0.24 are pure α-phase and samples with x=0.52 and 0.83 contain both α- and β-phase. The sample with x=0.52 has α-phase in 0.77 part of the volume and β-phase in 0.33 part of the volume. The sample with x=0.83 has α-phase in 0.25 part of the volume and β-phase in 0.75 part of the volume. The concentration dependences of the lattice parameters of crystal structures of different phases, obtained at room temperature in [1] for the $K_{1-x}(NH_4)_xBr$ mixed crystals and at low temperature in recent investigation, are presented in Fig. 3. The results of [1] show that on x-T phase diagram of $K_{1-x}(NH_4)_xBr$ at room temperature with x=0.613 both α- and β-phases are presented and we have two-phase compound. In accordance with our results two-phase compounds in $K_{1-x}(NH_4)_xBr$ system at 23 K (α- and β-phases) are observed within concentration region $0.52<x<0.82$.

The IINS and G(E) spectra for KRb and $K_{0.95}(NH_4)_{0.05}Br$ are presented in Fig. 4 and Fig. 5 respectively. Earlier these results were published in [4]. The comparison of the IINS spectra from KBr (at 80 K) and from $K_{0.95}(NH_4)_{0.05}Br$ (at 10 K) show the changes which appeared in vibrational spectrum of mixed crystal for a number of ammonium orientational degrees of freedom. First change is connected with the appearance of local vibrations with energies more than boundary energy in vibrational spectrum of KBr. There are translational mode ν_5 with the energy 24.3 meV and librational mode ν_6 with the energy 35.4 meV. Second change is the appearance of resonance hydrogen mode E_r^1 with the energy 2.1 meV on the background of strong contribution of the quasielastic incoherent neutron scattering (QINS) on the wings of elastic scattering profile from analyzing crystals. The QINS contribution in the IINS spectrum of $K_{0.95}(NH_4)_{0.05}Br$ mixed crystal at low temperature shows the presence of orientation disorder behavior of ammonium ions which confirms disorder crystal structure of α-phase in this concentration region. The comparison of the G(E) spectra of KBr and $K_{0.95}(NH_4)_{0.05}Br$ mixed crystal show all peculiarities in the difference of both spectra pointed in earlier comparison of the IINS spectra except the appearance of second resonance mode with energy E_r^2 near 10 meV observed in the $K_{1-x}(NH_4)_xI$ mixed crystals.

The continuation of the study of the $K_{1-x}(NH_4)_xBr$ mixed crystals with x=0.14, 0.24, 0.52, 0.83 and 1.0 at T=23 K was carried out. The obtained IINS and calculated G(E) spectra for these samples are presented in Fig. 6 and Fig. 7 respectively. If the IINS and G(E) spectra for the samples with x=0.14 and 0.24 are suit to the one-phase $K_{1-x}(NH_4)_xBr$ mixed crystals with crystal structures of α-phase so for the samples with x=0.52 and 0.83 that spectra are suit to two-phases $K_{1-x}(NH_4)_xBr$ mixed crystals with crystal structures of α- and β-phases. The IINS spectra of the samples with x=0.14 and 0.24 show following peculiarities. There are the contributions of the QINS which is diminish with increasing of ammonium concentration and such behaviour can be explained as the orientational glass state formation process. The analysis of G(E) spectra gives the possibility to determine the changes in vibrational spectrum which are observed in the $K_{1-x}(NH_4)_xBr$ with ammonium concentration. There are selected resonance modes E_r^1 and E_r^2, local translational mode ν_5 and librational mode ν_6 in α-phase and local translational mode ν_5 and librational mode ν_6 in β-phase for x=0.52 and 0.83. It is worth to note the splitting of local librational mode ν_6 in β-phase on two sub-bands. Other interest peculiarity of the G(E) spectrum of $K_{0.17}(NH_4)_{0.83}Br$ mixed crystal is the appearance of Raman modes $\nu_5+\nu_6$ and $2\nu_6$ which are suit to β-phase. The G(E) spectrum of NH_4Br at 23 K is suit to crystal structure of δ-phase. The IINS and G(E) spectra of NH_4Br in different phases (at different temperatures) are presented in Fig. 8 and in Fig. 9 respectively. The lattice modes and Raman modes of NH_4Br at 22 K in δ-phase are presented in Fig. 10 by translational mode ν_5, librational mode ν_6 containing two sub-bands, and Raman modes $\nu_5+\nu_6$, $2\nu_6$, $\nu_5+2\nu_6$, $3\nu_6$ and $\nu_5+3\nu_6$.

The energies of selected lattice modes in α- and β-phases for the $K_{1-x}(NH_4)_xBr$ mixed crystals as a function of ammonium concentration and of lattice modes in δ-phase of NH_4Br are presented in Fig. 11.

Lattice dynamics calculations for δ-NH_4Br in the frame of valence force field (VFF) model were carried out (Fig.12) [7]. For the δ-NH_4Br dispersion curves have a complicated character and we can expect the splitting of the peaks on the DOS. Calculated energies on the boundaries of Brillouin zone are close to obtained experimental data.

Acknowlegments

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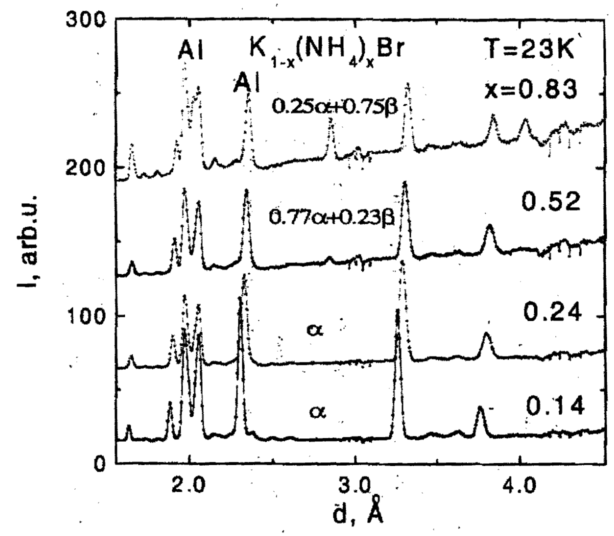

Fig. 1.

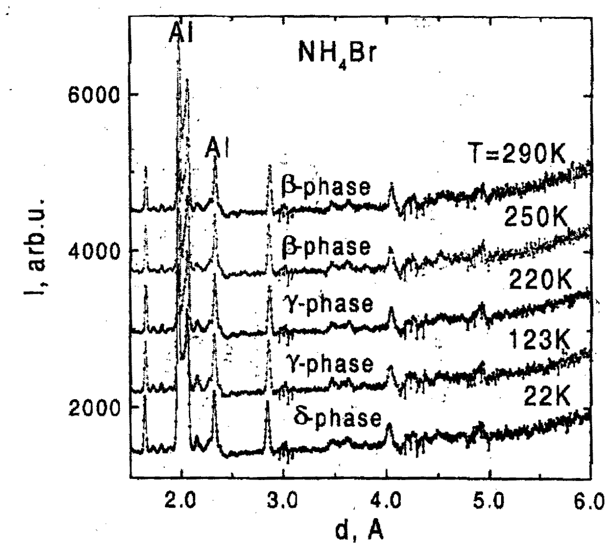

Fig. 2.

Fig. 1. The neutron powder diffraction spectra of the $K_{1-x}(NH_4)_xBr$ mixed crystals at 23 K.
Fig. 2. The neutron powder diffraction spectra of NH_4Br at different temperatures.

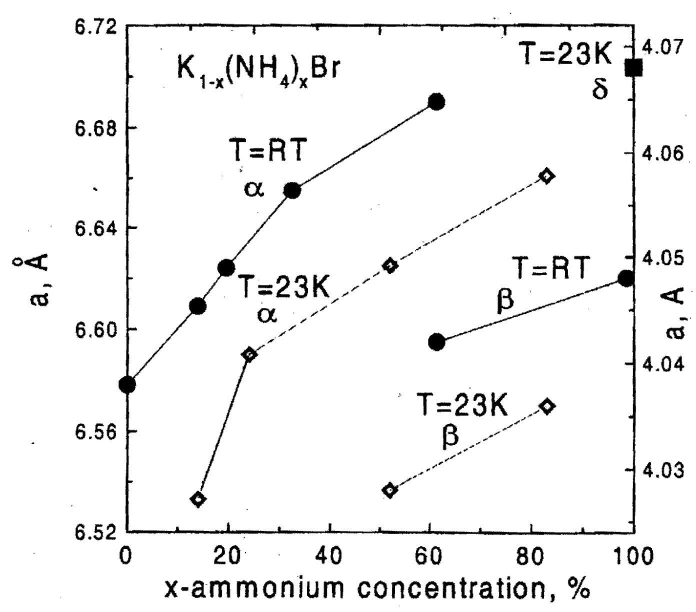

Fig. 3. The dependence of the lattice parameters of the $K_{1-x}(NH_4)_xBr$ mixed crystals as a function of ammonium concentration at room temperature and 23 K.

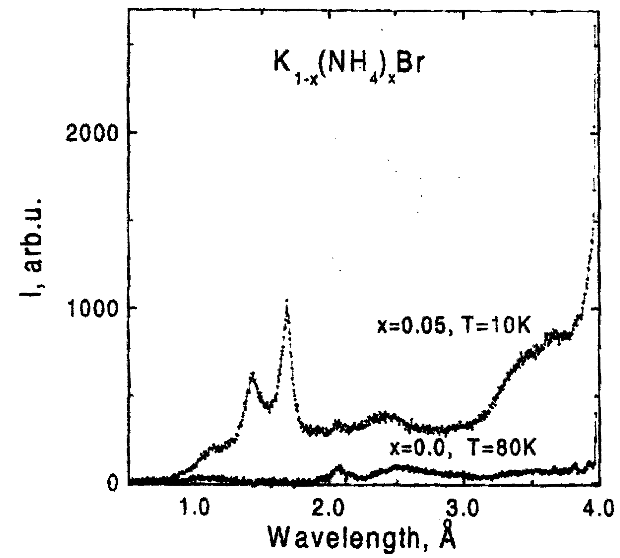

Fig. 4.

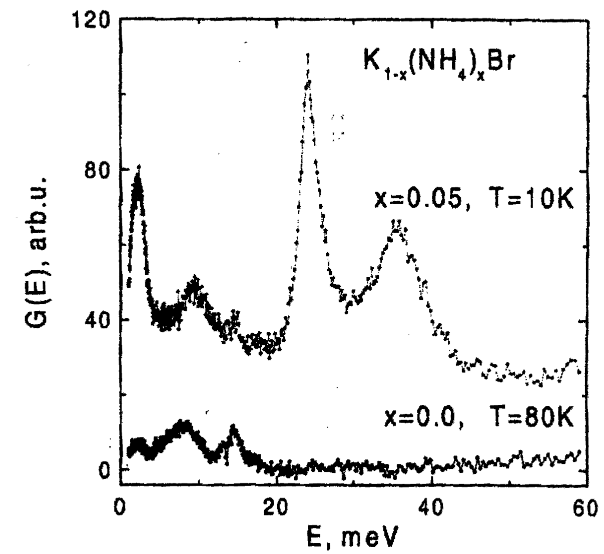

Fig. 5.

Fig. 4. The IINS spectra of KBr and $K_{0.95}(NH_4)_{0.05}$ at low temperature.
Fig. 5. The G(E) spectra of KBr and $K_{0.95}(NH_4)_{0.05}$ at low temperature.

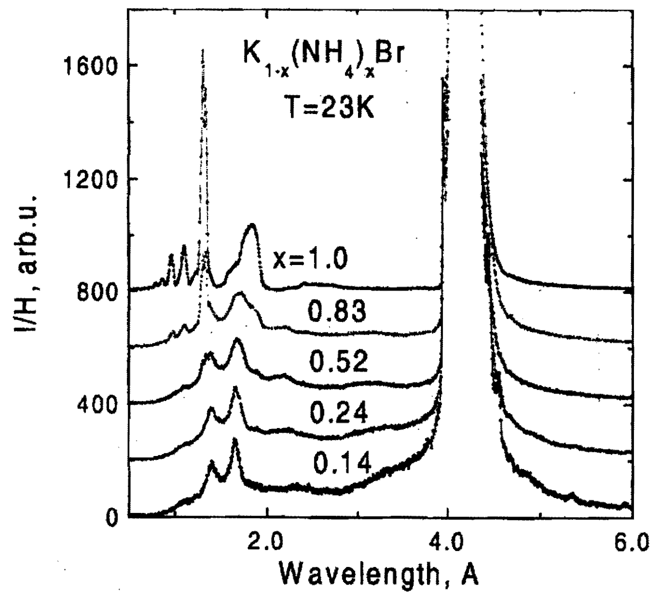

Fig. 6.

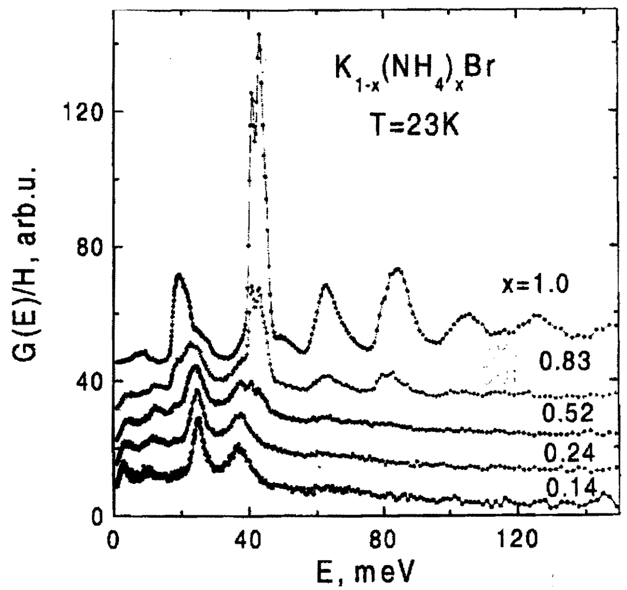

Fig. 7.

Fig. 6. The IINS spectra of the $K_{1-x}(NH_4)_xBr$ mixed crystals at 23 K.
Fig. 7. The G(E) spectra of the $K_{1-x}(NH_4)_xBr$ mixed crystals at 23 K.

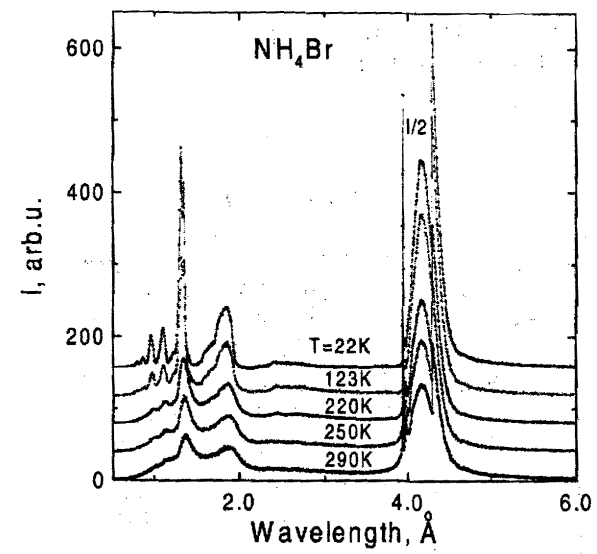

Fig. 8.

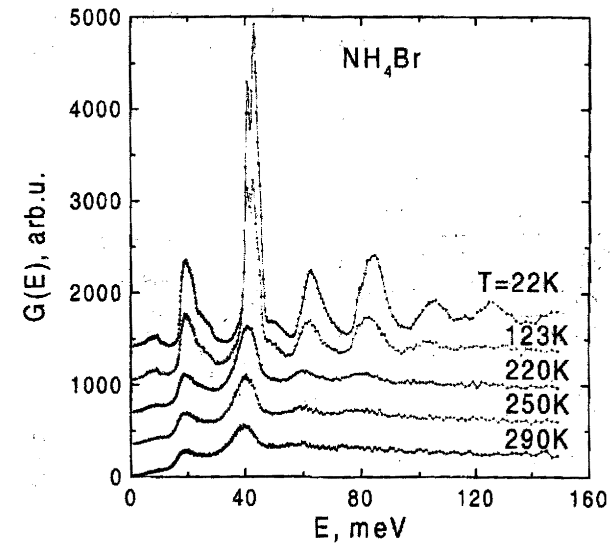

Fig. 9.

Fig. 8. The IINS spectra of NH_4Br at different temperatures.
Fig. 9. The G(E) spectra of NH_4Br at different temperatures.

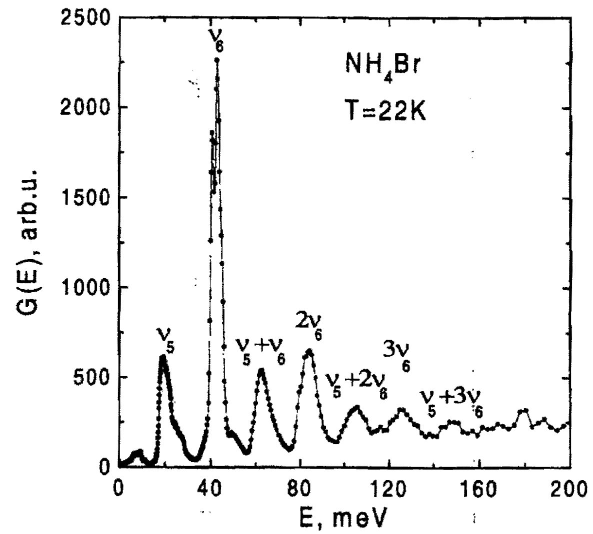

Fig. 10.

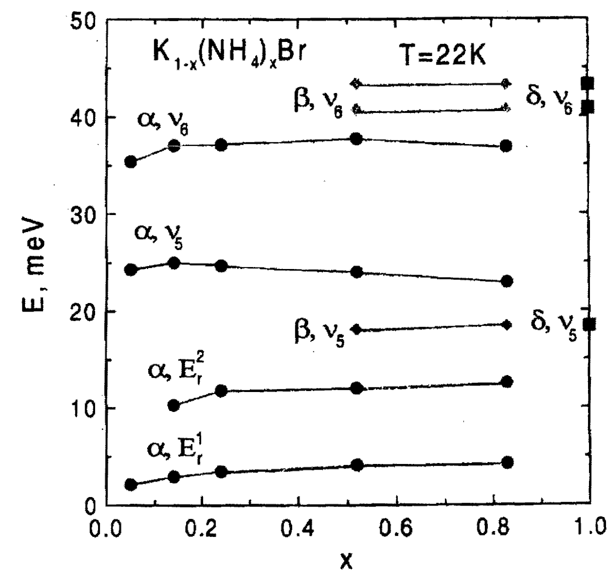

Fig. 11.

Fig. 10. The G(E) spectrum of NH_4Br at 22 K.
Fig. 11. The energies of modes in different phases of the $K_{1-x}(NH_4)_xBr$ mixed crystals.

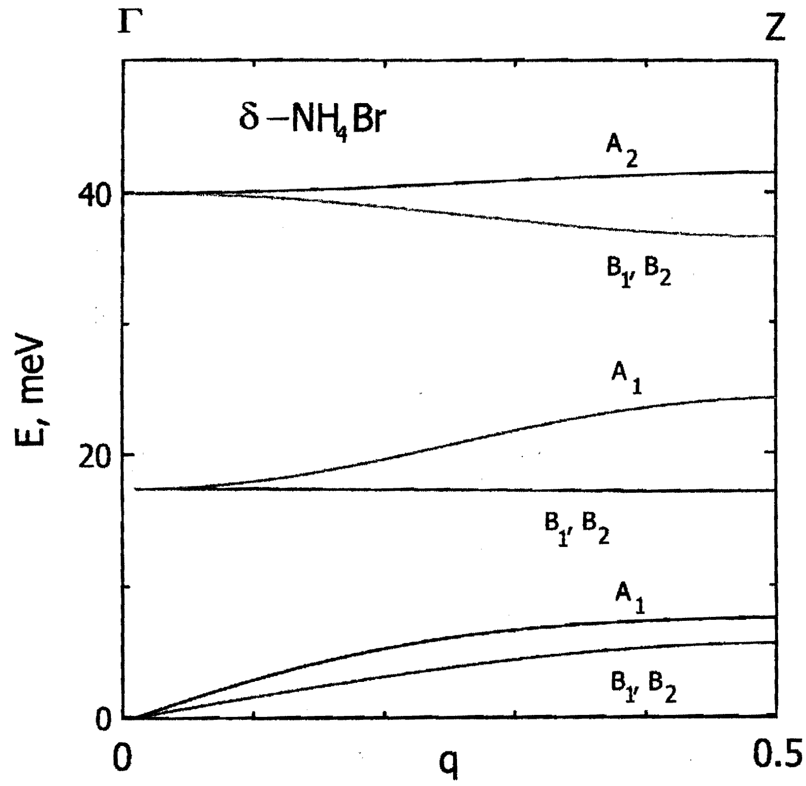

Fig. 12. Calculated dispersion curves (valence force field model) for δ-NH_4Br.

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