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L. S. Smirnov[1,2], I. Natkaniec[1,3], M. R. Johnson[4],
A. S. Ivanov[4], S. I. Troyanov[5]

# NEUTRON SCATTERING STUDY AND COMPUTER MODELING OF HYDROGEN VIBRATIONAL MODES IN $NH_4H_5(PO_4)_2$

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[1] Frank Laboratory of Neutron Physics, JINR, Dubna

[2] FSUE SSC RF A. I. Alikhanov Institute of Theoretical and Experimental Physics, 117218 Moscow

[3] H. Niewodniczanski Institute of Nuclear Physics, 31-342 Krakow, Poland

[4] Institut Max von Laue – Paul Langevin, BP 156-38042 Grenoble Cedex 9, France

[5] Moscow State University, Department of Chemistry, Vorobyevy Gory, 119992 Moscow

Смирнов Л. С. и др. E14-2006-114
Исследование с помощью рассеяния нейтронов и компьютерное
моделирование вибрационных мод водорода в $NH_4H_5(PO_4)_2$

Соединение $NH_4H_5(PO_4)_2$ принадлежит семье аддитивных комплексов 1:1 металловодородных фосфатов с фосфорной кислотой, описываемых общей формулой $MH_3PO_4$ $^{\bullet}H_2PO_4$, где $M$ = Na, K, Rb, Cs, $NH_4$ и Tl. Соединение $NH_4H_5(PO_4)_2$ представляет интерес ввиду трехмерной сети водородных связей между разными типами фосфатных тетраэдров и ионами аммония и как объект для исследования водородных мод таких водородных связей. Исследование с помощью неупругого некогерентного рассеяния нейтронов проведено на $NH_4H_5(PO_4)_2$ выше (при 220 K) и ниже (при 160 и 5 K) температуры фазового перехода (180 K). Значения энергии вибрационных мод кислотных водородов и водородов катионов аммония получены из измеренного спектра неупругого некогерентного рассеяния. Проведено компьютерное моделирование вибрационных мод для низкотемпературной фазы $NH_4H_5(PO_4)_2$ при 5 K. Вычисленные с учетом функции разрешения спектрометра IN1 BeF некогерентный динамический структурный фактор и парциальные вклады для всех водородов в интенсивность спектра неупругого некогерентного рассеяния нейтронов дают возможность провести идентификацию вибрационных мод от кислотных водородов и водородов катионов аммония.

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Препринт Объединенного института ядерных исследований. Дубна, 2006

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Smirnov L. S. et al. E14-2006-114
Neutron Scattering Study and Computer Modeling of Hydrogen
Vibrational Modes in $NH_4H_5(PO_4)_2$

The $NH_4H_5(PO_4)_2$ belongs to the family of addition 1:1 complexes of metal hydrogen phosphates with phosphoric acid, described by the general formula $MH_3PO_4$ $^{\bullet}H_2PO_4$, where $M$ = Na, K, Rb, Cs, $NH_4$ and Tl. The $NH_4H_5(PO_4)_2$ compound is presented by a three-dimensional framework of hydrogen bonds between different types of phosphate tetrahedra and ammonium ions and is an interesting object for the dynamic studies of such hydrogen bonds. The inelastic incoherent neutron scattering study is carried out from $NH_4H_5(PO_4)_2$ above (at 220 K) and below (at 160 and 5 K) the temperature of the phase transition (180 K). The energies of vibrational modes of acid hydrogens and hydrogens of ammonium cations are obtained from the measured inelastic incoherent neutron scattering spectrum. The computer modeling of vibrational modes for the low temperature phase of $NH_4H_5(PO_4)_2$ at 5 K is carried out. The calculated S(E) incoherent dynamic structural factor with the consideration of the resolution function of the IN1 BeF spectrometer and the partial contributions of all hydrogens to the intensity of the inelastic incoherent neutron scattering spectrum give the possibility for the identification of the observed modes from acid hydrogens and hydrogens of ammonium cations.

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

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# INTRODUCTION

The crystal structure of the ammonium salt, $NH_4H_5(PO_4)_2$, was first studied in [1] where only the structural data were briefly discussed without atomic coordinates. A detailed structural study was published in [2], where the results of X-ray single crystal diffraction study were presented. The authors observed the phase transition in $NH_4H_5(PO_4)_2$ at 180 K and determined structural data (space group and lattice parameters) and atomic positions of each phase, the high temperature phase at 220 K and the low temperature phase at 130 K.

The refinements of hydrogen positions in low and high temperature phases of $NH_4H_5(PO_4)_2$ were fulfilled in [3] by means of single crystal neutron diffraction at 80 and 298 K, respectively. The phase transition at 180 K was recognized as order–disorder. Finally, it was confirmed that the high temperature disordered phase has a monoclinic unit cell with space group (sp. gr.) $C2/c$, $Z = 4$ and lattice parameters $a = 10.156(4)$ Å, $b = 7.554(3)$ Å, $c = 9.507(4)$ Å, and $\beta = 100.7(14)^o$ and the low temperature phase is fully ordered with monoclinic syngony and space group $P2_1/c$, $Z = 4$ and lattice parameters $a = 10.040(4)$ Å, $b = 7.628(2)$ Å, $c = 9.558(3)$ Å, and $\beta = 102.51(4)^o$.

The high temperature phase consists of $NH_4^+$ cations and dimeric $[H(H_2(PO_4)_2]$ anions. The «acid» protons H(1)–H(3) occupy sites so that H(1) and H(2) are in general positions and H(3) atom is fixed on a two-fold axis in a special position, being responsible for a statistical disorder of this atom. The acid H(1) and H(2) hydrogen atoms are located in a usual asymmetric type of hydrogen bonds and acid H(3) hydrogen belongs to symmetric centered bonds in disordering state. The ammonium cation has nearly regular tetrahedral geometry and N atom is situated in an inversion center in the special position 4b, resulting in a disorder of the $NH_4^+$ cation. Hydrogen atoms of $NH_4^+$ are found to be disordered on five sites with occupation factors 0.5 for H(4) and H(5), and 0.333 for H(6)–H(8).

The transformation of $NH_4H_5(PO_4)_2$ from the high temperature phase with sp. gr. $C2/c$ below 180 K in the low temperature phase with sp. gr. $P2_1/c$ is accompanied by the disappearance of an inversion center and a two-fold axis with simultaneous saving of unit cell dimensions. As the result of such a symmetry change, H(3) atom participates in an asymmetrical H bond and ammonium cation is completely ordered in the structure of the low temperature phase.

The projection of crystal structure of $(NH_4)H_5(PO_4)_2$ on $X0Z$ plane in the high temperature phase is presented in Fig. 1($a$) and in the low temperature phase it is presented in Fig. 1($b$).

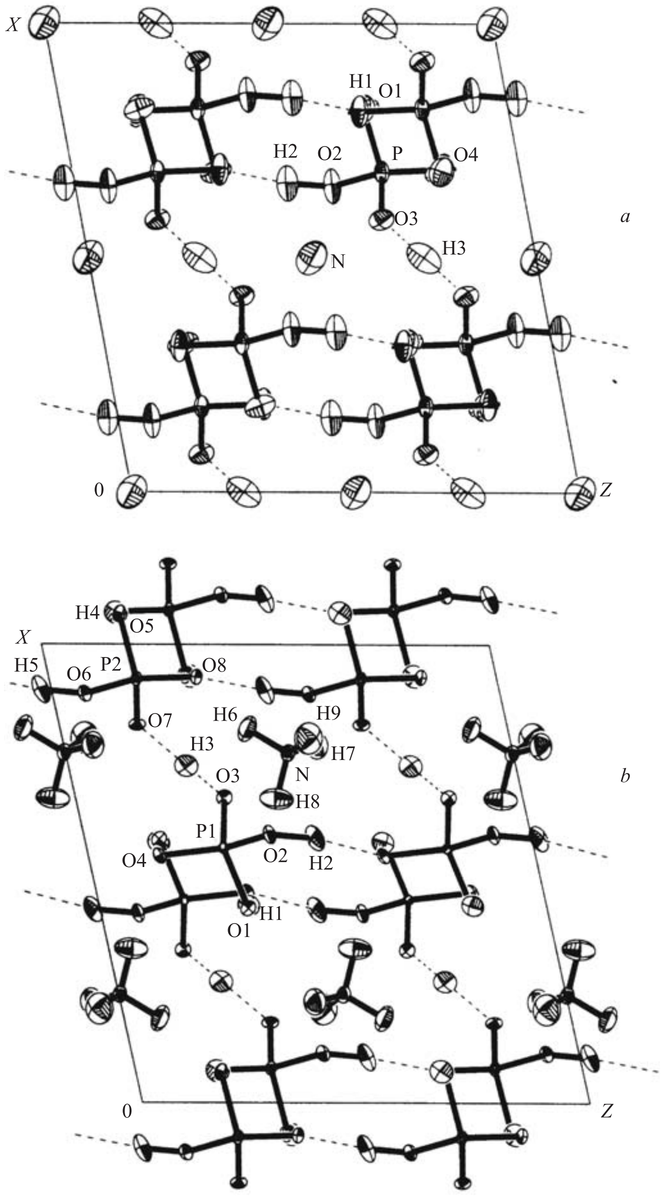

Fig. 1. The projection on $X0Z$ plane of crystal structure of $NH_4H_5(PO_4)_2$: ($a$) — high temperature phase, ($b$) — low temperature phase. The thermal ellipsoids are given with 50% probability, only hydrogen bonds of the type O–H. . . O are shown by dashed lines

The purpose of this communication is the presentation of results obtained during the study of the influence of the ordering of acid H(3) hydrogen atom and ammonium ions in the process of phase transition in $(NH_4)H_5(PO_4)_2$ by means of the inelastic incoherent neutron scattering.

## 1. EXPERIMENTAL DATA

Powder sample of $(NH_4)H_5(PO_4)_2$ is prepared in accordance with the description published in [2, 3]. The measurements of the inelastic incoherent neutron scattering (IINS) spectra from a powder sample were carried out on the IN1 BeF neutron spectrometer on the ILL reactor (Grenoble, France) at temperatures 5 and 160 K in the low temperature phase and 220 K in the high temperature phase. The obtained IINS spectra are presented in Fig. 2.

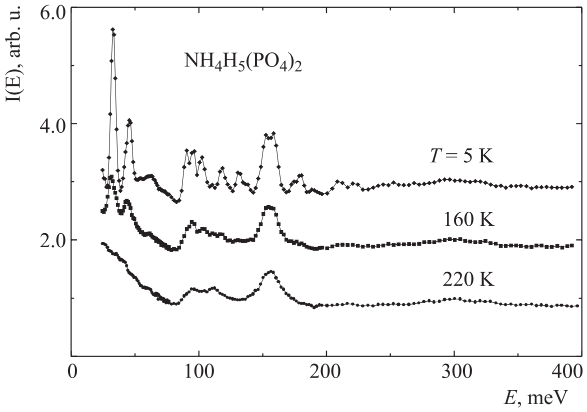

Fig. 2. $NH_4H_5(PO_4)_2$, obtained inelastic incoherent neutron scattering (IINS) spectra at 5 K and before and after phase transition at temperatures 160 and 220 K, respectively

It is worth noticing that the change of temperature affects significantly the IINS spectra of $NH_4H_5(PO_4)_2$. Firstly, increasing of the temperature from 5 to 160 K is accompanied by decreasing of the IINS intensity from the modes which could be related to librational motion and to the reorientation of ammonium ions. Secondly, at 220 K in the disordered high temperature phase the peaks in the IINS spectrum related to the inelastic incoherent neutron scattering from the modes of ammonium ions transform into the contribution of quasielastic incoherent neutron scattering intensity due to ammonium dynamic disorder and broadening related to the anharmonicity of librational motion of ammonium ions. Then, the presented peaks in the IINS spectrum of $NH_4H_5(PO_4)_2$ at 220 K could be connected with inelastic neutron scattering from modes of acid hydrogen atoms. Modeling calculation of the IINS spectrum from $NH_4H_5(PO_4)_2$ is performed in order to identify in detail the modes which contribute to the IINS spectrum of the low temperature phase of $NH_4H_5(PO_4)_2$.

## 2. COMPUTER MODELING

The vibrational spectra of the $NH_4H_5(PO_4)_2$ low temperature phase are calculated in harmonic approximation for all possible 240 modes without symmetry limitations. The methods and programs used for the dynamic calculations are described in the publications devoted to different compounds [4–10]. A full crystal calculation is performed using the *ab initio* total-energy and molecular dynamics program VASP (Vienna *ab initio* simulation program) [5–7]. The calculations are performed in reciprocal space, using a maximum $k$-point spacing of 0.01 $Å^{-1}$. Exchange-correlation effects are handled within the generalized gradient approximation (GGA–PBE).

First derivatives in the form of Hellmann–Feyman forces are available for all atoms in the cell by means of VASP. The force constant matrix is constructed from single point energy (SPE) calculations by displacing each of the symmetry inequivalent atoms in positive and negative senses along the Cartesian directions $x, y, z$ by 0.05 Å. A displacement of this size typically causes a restoring force of $\sim$ 0.5 eV/Å, ensuring that, generally, the induced forces are significantly greater than the numerical noise, while remaining in the regime of linear restoring forces. Each pair of SPE calculations (positive or negative displacements) enables a row of the force constant matrix, corresponding to a Cartesian displacement of one atom, to be determined, each force constant being a central difference $[(F^{+}–F^{-})/2\delta]$. Space group symmetry is used to relate the force constants within the matrix. Convergence of the calculation of force constants is tested as a function of the plane wave energy cutoff, $k$-point spacing, and the displacement size $\delta$. No significant improvement could be obtained using values different to those quoted above.

From force constant matrices vibrational frequencies and eigenvectors are calculated for $(NH_4)H_5(PO_4)_2$ by diagonalizing the dynamical matrix constructed with the corresponding mass matrix. Inelastic incoherent neutron scattering spectra, including overtones, combinations (including combinations with lattice modes) are calculated from the normal modes using the PHONON program [10].

The hydrogen atoms have a huge cross section of incoherent neutron scattering in comparison with that of other atoms. Therefore, common dynamic structural factor S(Q,E) for $(NH_4)H_5(PO_4)_2$ can be calculated taking into account only the incoherent scattering cross section from hydrogen atoms. As the result of averaging over scattering angles, in order to obtain the scattering for powder sample, and integral convolution of S(Q,E) with a resolution function of the IN1 BeF spectrometer, S(E) incoherent dynamic structural factor is obtained. The comparison of S(E), calculated for low temperature phase of $(NH_4)H_5(PO_4)_2$, and the IINS(E) spectrum, measured at 5 K, is presented in Fig. 3.

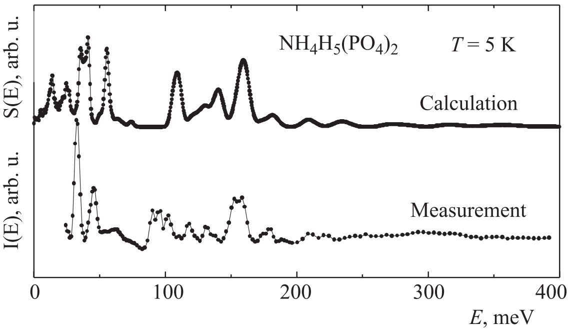

Fig. 3. The comparison of the IINS(E) spectrum of $NH_4H_5(PO_4)_2$, measured at 5 K, and S(E) spectrum, calculated for low temperature phase

Partial S(E) spectra for acid hydrogen atoms of dimers H($i$) ($i$ = 1,. . . 5) and partial S(E) spectra for hydrogen atoms of ammonium cation H($i$) ($i$ = 6,. . . 9) are calculated and presented in Fig. 4 ($a, b$).

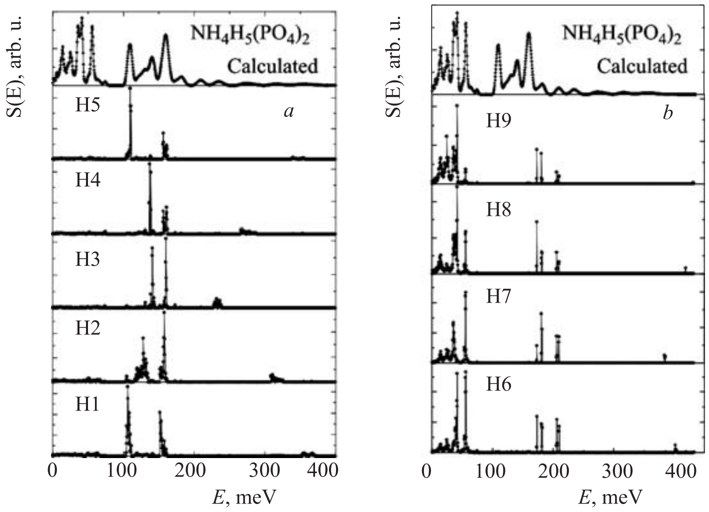

Fig. 4. ($a$) The partial contributions from H(1)–H(5) acid hydrogen atoms to common calculated S(E) spectrum for $NH_4H_5(PO_4)_2$; ($b$) the partial contributions from H(6)–H(9) ammonium hydrogen atoms to common calculated S(E) spectrum for $NH_4H_5(PO_4)_2$

## 3. DISCUSSION AND CONCLUSION

The comparison of the IINS(E) spectrum of $NH_4H_5(PO_4)_2$ at 5 K with the calculated S(E) spectrum for the low temperature phase (Fig. 3) shows that these spectra are almost analogous, but the calculated S(E) spectrum has a small shift to higher energy. The peaks of the S(E) spectrum are formed by scattering from hydrogen modes which in accordance with the calculations by the PHONON program [10] have the partial contributions with the largest intensities among different hydrogen modes (Fig. 4). The choice of the hydrogen modes which contribute to the S(E) spectrum with maxima intensities is presented in the table below with corresponding identification.

**Possible assignment for determined vibrational modes in $NH_4H_5(PO_4)_2$ (energy in meV)**

| Experiment | | Model calculation | | | |
|---|---|---|---|---|---|
| IINS, $T = 5$ K | IINS, $T = 220$ K | H mode | Assignment | $PO_4$, $NH_4$ | Assignment |
| 33 | | | | | |
| | | 35.5 | H7 | | |
| | | 36.7 | H9 | | |
| | | 37.2 | H8 | | |
| | | 39 | H6 | | |
| | | 41.3 | H6, H8, H9 | | |
| 45.2 | | | | 44.4 | $\nu_2$–$PO_4$ |
| | | 49.6, 53.6 | H9 | | |
| 53.3 | | | | | |
| | | 55.3 | H7, H8 | | |
| | | 55.4 | H6 | | |
| 60.8 | | | | | |
| | | | | 62 | $\nu_4$–$PO_4$ |
| 90.5 | | | | | |
| 95.6 | 93.9 | | | | |
| 101.9 | | | | | |
| | | 104.5 | H1 | | |
| | 110 | 106, 108 | H2 | | |
| | | 110 | H5 | | |
| 118 | | 119, 123.5, 128 | H1 | 120.3 | $\nu_1$–$PO_4$ |
| | | 131 | H3 | | |
| 131.6 | | 131.8 | H1 | 134 | $\nu_3$–$PO_4$ |
| 137.6 | | 137.6 | H4 | | |
| | | 141 | H3 | | |

| | | | | | |
|---|---|---|---|---|---|
| 152.5 | | 152.6 | H2 | | |
| | | 153 | H1 | | |
| | 156 | 157 | H2 | | |
| | | 158.2 | H5 | | |
| 159.2 | | 159.6 | H4 | | |
| | | 160 | H3 | | |
| | | 172.6 | H7, H8, H9 | | |
| | | 173 | H6 | | |
| 178.3 | | | | 179 | $\nu_4$–$NH_4$ |
| | | 180.4 | H9 | | |
| | | 180.7 | H7 | | |
| | | 181 | H8 | | |
| | | 181.4 | H6 | | |
| | | | | 205 | $\nu_2$–$NH_4$ |
| | | 205.6 | H7, H8, H9 | | |
| | | 206 | H6 | | |
| | | 209.5 | H7, H8, H9 | | |
| | | 210 | H6 | | |
| 214.4 | | | | | |
| | 217 | 230, 235 | H3 | | |
| 247 | | | | | |
| | 248 | | | | |
| 251.2 | | | | | |
| | | 267.6, 278.7 | H4 | | |
| 297.4 | | | | | |
| | 302 | | | | |
| 320.2 | | 310.4, 316.5, 320.9 | H1 | | |
| | | 340, 352.6 | H5 | | |
| | | 355.8, 366.6 | H2 | | |
| | | 368 | H7 | | |
| | | | | 395 | $\nu_1$–$NH_4$ |
| | | 402, 402.8 | H6 | | |
| | | | | 412 | $\nu_3$–$NH_4$ |
| | | 417 | H8 | | |

Thus, the modeling calculation of the vibrational spectrum of the low temperature phase of $NH_4H_5(PO_4)_2$ shows the positions of acid hydrogen atoms and hydrogen atoms of ammonium cation. The disappearance in the IINS(E) spectrum of contributions from hydrogen modes of ammonium cations confirms the result of the determination of crystal structure of $NH_4H_5(PO_4)_2$ obtained by X-ray and neutron single crystal diffraction [2, 3] and the nature of the phase transition in this substance to be an order–disorder transition.

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141980, г. Дубна, Московская обл., ул. Жолио-Кюри, 6.
E-mail: publish@jinr.ru
www.jinr.ru/publish/