

RESEARCH ARTICLE

Raman scattering and phase transitions in $(\text{NH}_4)_3\text{TiF}_7$

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Abstract

Raman spectra of $(\text{NH}_4)_3\text{TiF}_7$ within spectral range 10–3,400 cm^{-1} at temperatures 8–370 K are recorded, which revealed 2 phase transitions at temperatures $T_1 = 355$ K and $T_2 = 283$ K. First principles calculations of lattice dynamics and assignment of the observed lines to specific vibrational types are performed. The first phase transition is classified as an “order–disorder” one. Manifestation of 97 cm^{-1} vibration (mixed translational $[\text{NH}_4 + \text{F}7]$) evidences the creation of the hydrogen bond between ammonium group and free fluorine atom, indicating to reconstructive type of phase transition at $T_2 = 283$ K. The emergence of a large number of vibrational lines in Raman spectra at low temperatures proves symmetry lowering of NH_4 tetrahedra with the simultaneous ordering of TiF_6 octahedra.

KEYWORDS $(\text{NH}_4)_3\text{TiF}_7$, lattice dynamics, order–disorder, reconstructive phase transition, symmetry lowering

1 | INTRODUCTION

Titanium fluoride double salt $(\text{NH}_4)_3\text{TiF}_7 = (\text{NH}_4)_2\text{TiF}_6 \cdot \text{NH}_4\text{F} = (\text{NH}_4)_3[\text{TiF}_6]\text{F}$ is the main product of fluoride processing of titanium-containing raw materials (ilmenite and rutile) when ammonium hydrogen difluoride (NH_4HF_2) is used as fluorinating agent to produce pigmentary titanium dioxide (TiO_2).^[1–5] Marignac^[6] was the first who described this compound back in 1859.

Correction added on 27 April 2018, after first online publication: Author's name has been corrected from “E.M Roginsky” to “E.M Roginskii”. Affiliation 5 has been corrected from “Ioffe Physical Technical Institute” to “Ioffe Institute”.

Only recently, its crystal structure was studied by Molochev et al.^[7] The compound crystallizes in tetragonal syngony (space group $P4/mnc$) at room temperature. The crystal structure incorporates three independent TiF_6 octahedra, one of them, $\text{Ti}3\text{F}_6$, is disordered among four positions. The disordering looks like the gyration of the pseudo-three-fold axis of the octahedron $\text{Ti}3\text{F}_6$ around the fourfold axis of the crystal. Two independent ammonium ions are coordinated by two and three TiF_6 polyhedra.

Optical and differential scanning calorimetric investigations have shown that $(\text{NH}_4)_3\text{TiF}_7$ undergoes two reversible first-order structural transformations.^[8] An unusual succession of two structural phase transitions

was observed upon heating and cooling $P4/mbm \xrightleftharpoons{361\text{ K}} P4/mnc \xrightleftharpoons{293\text{ K}} Pa\bar{3}$. Maxima of the heat capacity peaks were located at the temperatures $T_1 = 361 \pm 2.0\text{ K}$ and $T_2 = 293 \pm 1.0\text{ K}$. The sum of entropies associated with both phase transitions is rather large: $\sum \Delta S_i = \Delta S_1 + \Delta S_2 = 32 \pm 2\text{ J/mol K}$.^[9] Individual values of entropy change in $(\text{NH}_4)_3\text{TiF}_7$ differ from each other significantly: $\Delta S_1 = 9.2 \pm 0.6\text{ J/(mol K)}$ ($\sim R \ln 3$), $\Delta S_2 = 22.7 \pm 1.6\text{ J/(mol K)}$ ($\sim R \ln 16$). The very large ΔS_2 value is the result of large atomic displacements in the reconstructive transformation. Moreover, the phase transition at T_2 was accompanied by the reversible cracking of crystals observed in polarizing-optic measurements, which allowed it to be considered a reconstructive transformation.^[8] During such transformation, total restructuring of hydrogen bonds occurs. Breaking of hydrogen bonds and creating new ones take place.^[7]

The aim of the current study is to investigate the unusual reconstructive phase transition in the $(\text{NH}_4)_3\text{TiF}_7$ crystal using Raman spectroscopy.

2 | EXPERIMENTAL

2.1 | Synthesis

The starting substances for the synthesis of $(\text{NH}_4)_3\text{TiF}_7$ were solid $(\text{NH}_4)_2\text{TiF}_6$ and concentrated solution of NH_4F (40 wt%) of a reagent grade. The threefold excess of NH_4F was used relative to the reaction: $(\text{NH}_4)_2\text{TiF}_6 + \text{NH}_4\text{F} = (\text{NH}_4)_3\text{TiF}_7$. 10–11 g of $(\text{NH}_4)_2\text{TiF}_6$ were added to 50 mL of hot solution of NH_4F (pH ~ 7 –8). Upon cooling to room temperature, a polycrystalline precipitate of titanium fluoride double salt was obtained, which was filtered, washed with cold water and alcohol, and air dried. From the mother liquor, transparent single crystals of $(\text{NH}_4)_3\text{TiF}_7$ in the form of tetragonal prisms or cubes were formed, which were also used for Raman experiments.

2.2 | Spectral acquisition

The unpolarized Raman spectra were collected in a back-scattering geometry, using a triple monochromator Horiba Jobin Yvon T64000 Raman spectrometer operating in double subtractive mode, and detected by a LN-cooled charge-coupled device. Single-mode argon 514.5 nm from a Spectra-Physics Stabilite 2017 Ar^+ laser of 5 mW on the sample was used as excitation light source. The intensity of the laser light was adjusted to avoid sample heating.

Temperature measurements were carried out using a closed cycle ARS CS204-X1.SS helium cryostat in the temperature range of 8–370 K. The temperature was

monitored by using a LakeShore DT-6SD1.4 L silicon diode. During experiments, the cryostat was evacuated to 10^{-6} mbar. To investigate the low-wavenumber spectra, measurements down to 10 cm^{-1} were performed in a subtractive dispersion mode. Deformation of the low-wavenumber spectral edge by the optical slit, which sometimes smears the true features of the low-wavenumber spectra, was carefully eliminated by rigorous optical alignment. The CCD pixel coverage in an additive dispersion mode was as fine as 0.3 cm^{-1} , but it was limited by the spectrometer spectral resolution of 1.8 cm^{-1} .

The temperature experiments were carried out in a dynamic mode^[10,11] varying the sample temperature at the rate of 0.7 K min^{-1} . The uncertainty of the measured temperature for a given rate can be estimated as the difference between the adjacent measurements, and it was $\pm 0.35\text{ K}$ in one spectrum measurement. The overall time for a single spectrum accumulation was within 60 s. The spectra were acquired with a temperature step of 0.7 K. The ammonium region have weaker spectrum, so measurement parameters have increased values: Temperature step was 2 K, spectrum accumulation time was 100 s, and uncertainty was $\pm 0.9\text{ K}$.

2.3 | Density functional theory calculations

To interpret the observed Raman spectra, quantum chemical calculation of the structure and vibrational spectra of the low temperature phase of $(\text{NH}_4)_3\text{TiF}_7$ at density functional theory level using CASTEP program package were made.^[12] Initial structure of the low-temperature cubic phase $Pa\bar{3}$ was completely optimized using either local density approximation (LDA)^[13] or generalized gradient approximation (GGA) with Perdew-Burke-Ernzerhof (PBE) exchange functional.^[14] Calculations were carried out using norm-conserving pseudopotentials for electronic configurations $1s^1$ (hydrogen), $2s^2 2p^3$ (nitrogen), $2s^2 2p^5$ (fluorine), and $3s^2 3p^6 3d^2 4s^2$ (titanium). Optimization of intracell atomic positions was carried out under following convergence limits: $5.0 \cdot 10^{-8}\text{ eV}$ per atom for energy, 0.01 eV/\AA for forces, 0.02 GPa for compression, and $5.0 \cdot 10^{-4}\text{ \AA}$ for displacement. The value of limiting cutoff of plane waves E_{cut} was chosen to be 1,000 eV. Integration over the Brillouin zone was done by the method of special points^[15] on $2 \times 2 \times 2$ and $3 \times 3 \times 3$ grids. Phonon spectrum was calculated using perturbation theory of density functional.

3 | RESULTS AND DISCUSSION

Raman spectra of $(\text{NH}_4)_3\text{TiF}_7$ in the range of vibration of the TiF_6 octahedral group recorded at different

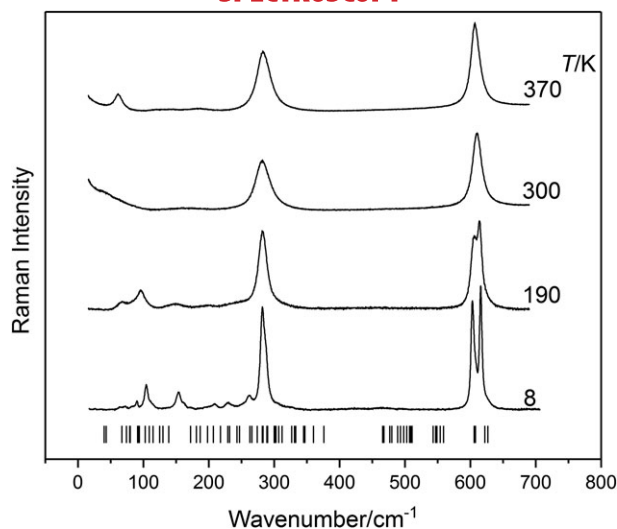


FIGURE 1 Raman spectra of $(\text{NH}_4)_3\text{TiF}_7$ in the range of TiF_6 and lattice vibrations at different temperatures. DFT-calculated Raman-active zone-center phonon wavenumbers are shown by vertical ticks

temperatures are presented in Figure 1. The Raman intensity maps and temperature transformation of internal bending and stretching vibrations of ammonium ions are shown in Figures 2 and 3, respectively.

The lattice parameter of $(\text{NH}_4)_3\text{TiF}_7$ structure optimized using LDA approximation (11.414264 Å) is 3.1% lower, whereas that obtained using GGA (PBE) approximation (12.104707 Å) is 2.73% larger, than the experimentally measured value at 143 K (11.78287 Å),^[7] which is in agreement with the general tendency that LDA underestimates, whereas GGA (PBE) overestimates lattice parameters.^[16] Calculation of phonon spectrum using both LDA and GGA approximations revealed no modes with imaginary wavenumbers, which evidences the stability of $Pa\bar{3}$ structure down to 0 K. Calculated phonon spectrum in the range 1,350–1,700 cm^{-1} corresponds to the bending

NH_4 vibrations, and the 2,570–3,260 cm^{-1} range contains stretching vibrations of N–H bonds. Internal vibrations of TiF_6 octahedra are located in the range of 120 – 650 cm^{-1} .

Lattice modifications connected with phase transitions are well pronounced in experimental Raman spectra. Vibrational modes observed at different temperatures together with their assignments are listed in Table 1.

Crystal structure data for both room- and low-temperature phases of $(\text{NH}_4)_3\text{TiF}_7$ ^[7] should be used for more detailed interpretation of the changes ongoing in Raman spectra. The room-temperature structure contains three independent TiF_6 octahedra. One of them denoted as Ti3F_6 , which is orientationally disordered between four positions, becomes ordered in low temperature (cubic) phase, whereas two other octahedra Ti1F_6 and Ti2F_6 rotate relatively to the initial orientation by a large angle. This means that a reconstructive phase transition takes place at 292.5 K.^[7] Additionally, the number of hydrogen bonds in $P4/mnc$ is different from that in $Pa\bar{3}$, also indicating a significant reconstruction during the phase transition.

Low-temperature phase demonstrates two peaks in the 600 cm^{-1} range, which corresponds to fully symmetric TiF_6 stretching vibrations (see spectrum at 190 K in Figure 1). According to lattice dynamics calculations, the 614- cm^{-1} peak corresponds to a Ti2F_6 vibration, whereas the 606 cm^{-1} peak is assigned to Ti1F_6 . Internal ν_2 vibration of TiF_6 anion should be observed around 450 cm^{-1} ; however, its intensity is usually small in the Raman spectra, and they are visually not detected in our spectra. A single intense peak is observed at 282 cm^{-1} , which is assigned to ν_5 (F_{2g}) vibrations of Ti2F_6 and Ti1F_6 octahedra. The 200–250 cm^{-1} range contains translational vibrations of NH_4 . Rocking vibrations of NH_4 appear in the range of 150 cm^{-1} . The intense Raman peak at 97 cm^{-1}

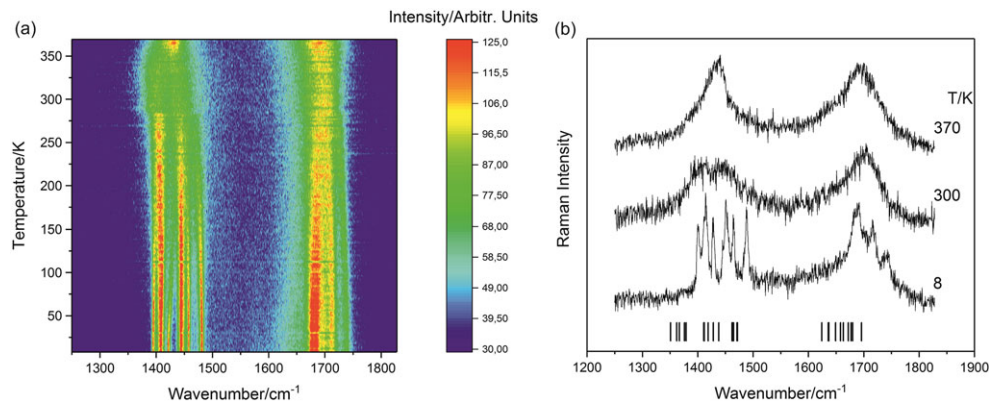


FIGURE 2 Raman intensity maps (a) and temperature transformation (b) of bending vibrations of ammonium ions in $(\text{NH}_4)_3\text{TiF}_7$. Density functional theory-calculated Raman-active zone-center phonon wavenumbers are shown by vertical ticks [Colour figure can be viewed at wileyonlinelibrary.com]

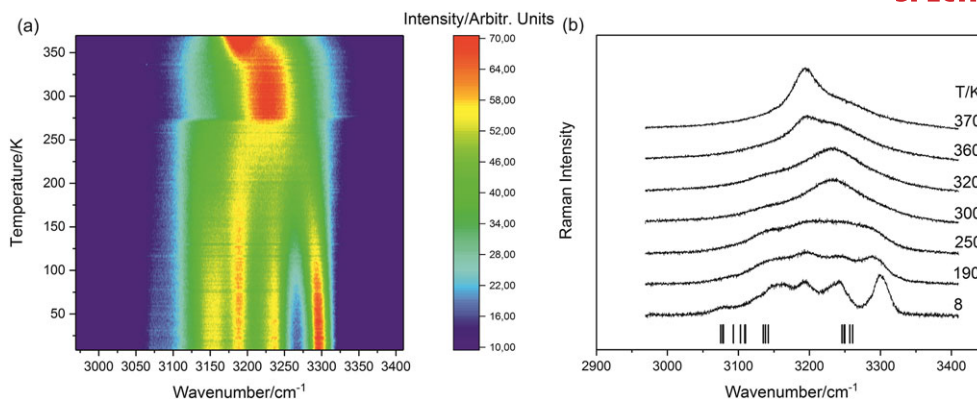


FIGURE 3 Raman intensity maps (a) and temperature transformation (b) of stretching vibrations of ammonium ions in $(\text{NH}_4)_3\text{TiF}_7$. Density functional theory-calculated Raman-active zone-center phonon wavenumbers are shown by vertical ticks [Colour figure can be viewed at wileyonlinelibrary.com]

TABLE 1 Experimental Raman bands wavenumbers of different phases of $(\text{NH}_4)_3\text{TiF}_7$ and their assignments

8 K	190 K	300 K	370 K	Description
3,077; 3,128; 3,157; 3,192; 3,240; 3,299	3,077; 3,153; 3,194; 3,240; 3,286	3,142; 3,232	3,196; 3,258	ν_1, ν_3 NH_4 stretching
1,686; 1,716; 1,742	1,690; 1,712; 1,734	1700	1,692	ν_2 NH_4 bending
1,400; 1,414; 1,427; 1,446; 1,450; 1,464; 1,488	1,409; 1,452; 1,481	1,405; 1,448	1,436	ν_4 NH_4 bending
603	606	610	606	ν_1 TiF_6 stretching
615	614			
287; 281	282	282	283	ν_5 TiF_6 bending
261; 230	243		186	NH_4 translation
209	201			
153; 163;	150		124	NH_4 rocking
104; 90	97			NH_4 + F7 translation
64; 72	67		62	NH_4 transl. + TiF_6 rot.

is clearly seen in Figure 4; it is associated with the creating of the hydrogen bond between NH_4 group and free fluorine atom (F7)^[7]; this scenario is a characteristic for

reconstructive type of phase transition. Visualization of this vibrational mode is shown in Figure 5. Spectral line at 67 cm^{-1} corresponds to rotary vibration TiF_6 octahedra

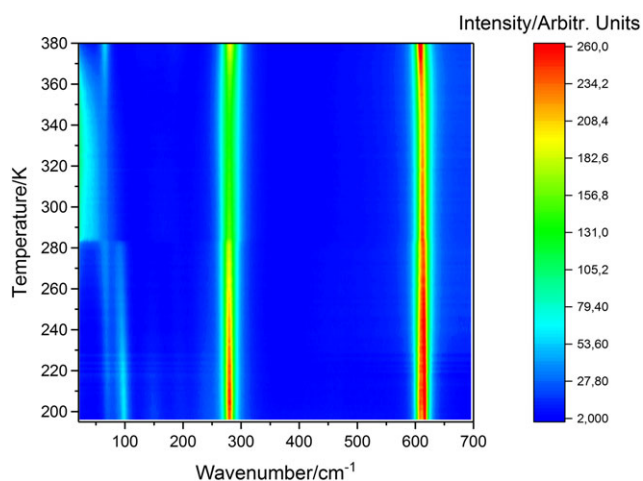


FIGURE 4 Raman intensity maps of $(\text{NH}_4)_3\text{TiF}_7$ spectra in the region of $20\text{--}700 \text{ cm}^{-1}$ [Colour figure can be viewed at wileyonlinelibrary.com]

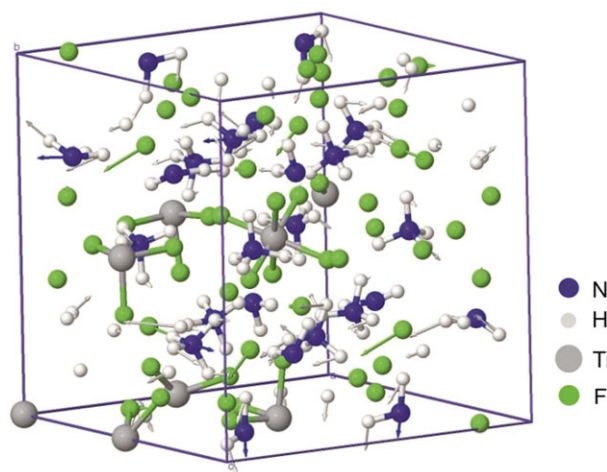


FIGURE 5 Simulated mixed translation of NH_4 groups and free fluorine atom (F7) related to Raman peak observed at 97 cm^{-1} [Colour figure can be viewed at wileyonlinelibrary.com]

and NH_4 displacement.^[17] Further cooling down to 8 K leads to minor shift of Raman bands and to increase in their intensities.

Raman spectrum of the $P4/mnc$ phase at 300 K (Figure 1; Table 1) contains two significantly wide bands assigned to TiF_6 vibrations, and also a Rayleigh wing of high intensity is observed. Translational and rocking vibrations of NH_4 are very weak. All these features indicate the structure disordering.

Further temperature increase above 360 K leads to yet another phase transition, and the structure of new high-temperature phase is identified as $P4/mbm$.^[7] The Rayleigh wing intensity is considerably decreased in this phase, and the 63 cm^{-1} line becomes clearer, which indicates less disorder of high-temperature phase in comparison with the room temperature phase. Spectral lines of TiF_6 octahedra are somewhat shifted relative to their position at 300 K.

At the Raman intensity map (Figure 2a), the changes associated with phase transitions at temperatures $T_1 = 355\text{ K}$ and $T_2 = 283\text{ K}$ are well seen in the region of internal deformation vibrations of tetrahedral ammonium groups ($1,200\text{--}1,900\text{ cm}^{-1}$). In Raman spectrum of $P4/mbm$ phase (Figure 2b; 370 K), two broad bands are pronounced that evidences disordering of tetrahedral groups. Room-temperature structure contains two translationally independent NH_4 tetrahedra; therefore, as a result, we must obtain two normal vibrations for each spectral range,^[18] which is in accordance with the experimental spectrum in Figure 2b (300 K). A single translationally independent tetrahedral NH_4 group of T_d symmetry is present in the low-temperature structure of $(\text{NH}_4)_3\text{TiF}_7$, and N—H bond length is equal to 0.9 \AA (Figure 6a).^[7] However, the optimization of the initial geometry^[7] gives the N—H bond lengths to be non-equal (Figure 6b). This leads to the removal of degeneracy. Spectral contour at 8 K can be divided into at least 10 peaks, whereas calculations predict 25 modes, part of them, as can be deduced from Figure 2b, is close enough to each other to be overlapped in the experimental spectra.

Spectral changes that are observable in the region of internal valence vibrations of ammonium ions ($3,000\text{--}$

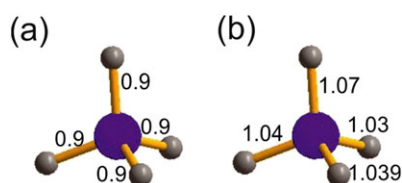


FIGURE 6 Interatomic distances in the NH_4 tetrahedron: (a) X-ray diffraction data, $T = 143\text{ K}$ ^[7]; (b) density functional theory calculation [Colour figure can be viewed at wileyonlinelibrary.com]

$3,400\text{ cm}^{-1}$) within $360\text{--}340\text{ K}$ temperature range are connected with the long-time kinetics of order–disorder phase transition, Figure 3a. Room temperature spectrum contains two bands corresponding to the symmetric and asymmetric valence vibrations of NH_4 , which allows deducing the fact that tetrahedra in the $P4/mnc$ phase are ordered. Below the temperature of the second phase transition, the changes are observed that are typical for those in case of lowering the symmetry of NH_4 group. Number of Raman active modes increases, and at 8 K, at least 6 peaks are well distinguishable, whereas calculations predict 15 modes (Figure 3b).

4 | CONCLUSIONS

Raman spectra of $(\text{NH}_4)_3\text{TiF}_7$ were obtained for the first time within spectral range $10\text{--}3,400\text{ cm}^{-1}$ at temperatures $8\text{--}370\text{ K}$ that revealed two phase transitions. It was experimentally established that the crystal structure of $Pa\bar{3}$ phase is stable down to 8 K, which is consistent with the results of the first-principle calculations.

The lines in the Raman spectra were identified and assigned by the types of vibrations of structural units. The mechanisms of phase transitions' implementation were established. It is shown that $P4/mbm \rightarrow P4/mnc$ is accompanied by disordering of TiF_6 octahedra evidenced by noticeable enlargement of the Rayleigh wing intensity: At the same time, NH_4 tetrahedra undergo ordering.

$P4/mnc \rightarrow Pa\bar{3}$ phase transition determined earlier as a reconstructive one is accompanied by ordering of TiF_6 octahedra and a symmetry lowering of NH_4 tetrahedra; the latter leads to the emergence of a large number of vibrational lines in the Raman spectra at low temperatures. Creating of the bonds between the free fluorine atoms and NH_4 groups ($\text{N}\cdots\text{H}\cdots\text{F}_3$, $d[\text{N}\cdots\text{F}] = 2.673\text{ \AA}$) leads to the emergence of mixed translational ($\text{NH}_4 + \text{F}_7$) vibration, which is manifested (reflected) at 97 cm^{-1} below the temperature of reconstructive phase transition.

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