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# Ferroelastic phase transition in the family of double fluoride crystals by Raman spectroscopy

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## ABSTRACT

In order to clarify ordering mechanisms of ferroic phase transitions in double fluoride salts  $(\text{NH}_4)_3\text{SnF}_7$ ,  $(\text{NH}_4)_3\text{GeF}_7$  and  $(\text{NH}_4)_3\text{TiF}_7$ , their Raman scattering spectra have been studied in wide ranges of frequencies ( $20\text{--}3400\text{ cm}^{-1}$ ) and temperatures ( $8\text{--}410\text{ K}$ ). Substitution of the central ion in the octahedron groups was found to change not only the phase transition types and sequences, but to modify the types of structural disorder as well, which is a special feature of these high-symmetry fluoride crystals.

## ARTICLE HISTORY

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## KEYWORDS

Fluorides; Raman spectra; lattice disordering

## 1. Introduction

There is a great difference in ionic radii of central atoms in the series of double fluoride salts  $\text{A}_3\text{F}[\text{MF}_6]$ , where  $\text{A} = \text{NH}_4, \text{K}, \text{Rb}, \text{Cs}$ ;  $\text{Me}^{4+}$ :  $\text{Si}, \text{Ge}, \text{Ti}, \text{Sn}, \text{Pb}, \text{Cr}, \text{Mn}, \text{Ni}$  [1–6]. As a consequence, temperature change can give rise to different sequences and mechanisms of structural distortions. The study of crystals of this family involves finding ways to realize ferroelectric phases. At room temperature, the phase symmetry of  $(\text{NH}_4)_2\text{SnF}_6 \cdot \text{NH}_4\text{F}$  and  $(\text{NH}_4)_2\text{GeF}_6 \cdot \text{NH}_4\text{F}$  heptafluoride single crystals differs from the one of  $(\text{NH}_4)_2\text{TiF}_6 \cdot \text{NH}_4\text{F}$ . A phase transition has been found in  $(\text{NH}_4)_2\text{SnF}_6 \cdot \text{NH}_4\text{F}$  with temperature rising above  $357\text{ K}$ , changing the symmetry from a cubic to another cubic phase:  $Pa-3$  (below  $357\text{ K}$ )  $\leftrightarrow$   $Pm-3m$  (above  $357\text{ K}$ ) [7]. Fluoride  $(\text{NH}_4)_3\text{GeF}_7 = (\text{NH}_4)_3\text{GeF}_6 \cdot \text{NH}_4\text{F}$  has been found to have the following structural phase transitions:  $P4/mbm$  ( $Z=2$ ) ( $T_1=279.4\text{ K}$ ) –  $Pbam$  ( $Z=4$ ) ( $T_2=270\text{ K}$ ) –  $P12_1/c1$  ( $Z=4$ ) ( $T_3=227\text{ K}$ ) –  $Pa-3$  ( $Z=8$ ) [8].

Two structural phase transitions have been found in  $(\text{NH}_4)_3\text{TiF}_7$  at  $T_1=358\text{ K}$  and  $T_2=287\text{ K}$  exhibiting an unusual sequence of symmetry changes:  $P4/mbm \rightarrow P4/mnc \rightarrow Pa-3$  [9–12]. Crystal lattice dynamics and mechanisms of structural phase transitions observed with changing temperature and pressure are traditionally studied with Raman scattering spectroscopy. The principal task of this study is a comparative analysis of spectral changes caused by phase transitions (PT) in these crystals.

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## 2. Experiment

Clear single crystals of stannum, germanium and titanium have been produced from aquatic solutions, the synthesis methods are described in [7–12]. When observed under microscope the crystals have not been found to have any visible flaws.

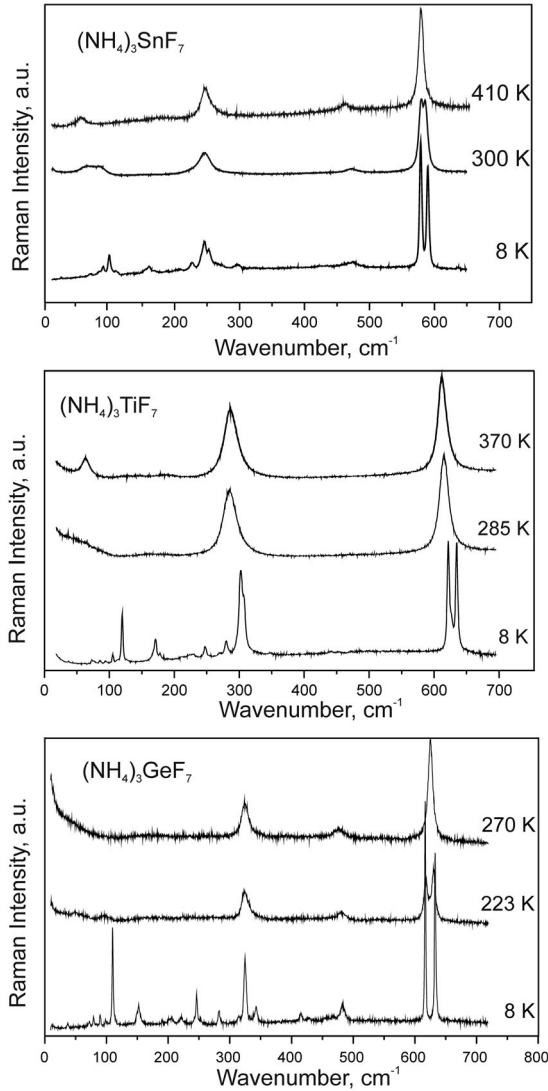
Raman scattering spectra of  $(\text{NH}_4)_3\text{SnF}_7$ ,  $(\text{NH}_4)_3\text{GeF}_7$ ,  $(\text{NH}_4)_3\text{TiF}_7$  have been studied in the temperature range from 8 K to 410 K. Raman spectra were collected in backscattering geometry with a triple monochromator Jobin Yvon T64000 Raman spectrometer operating in double subtractive mode, then detected by a liquid nitrogen-cooled CCD at 140 K. The spectral resolution for the recorded Stokes side Raman spectra was about  $2\text{ cm}^{-1}$  (this resolution was achieved by using 1800 grooves/mm gratings and  $100\ \mu\text{m}$  slits) with a low-frequency limit of  $10\text{ cm}^{-1}$  in the present setup. The deformation of the low-frequency spectral edge by an optical slit, which sometimes smears the true features of the low-frequency spectra, was carefully eliminated by rigorous optical alignment. Single-mode argon 514.5 nm of Spectra-Physics Stabilite 2017  $\text{Ar}^+$  100 mW laser (10 mW on the sample) was used as excitation light source for  $(\text{NH}_4)_3\text{SnF}_7$ ,  $(\text{NH}_4)_3\text{TiF}_7$  and single-mode krypton 647.1 nm of Lelux 95L  $\text{Kr}^+$  150 mW laser (15 mW on the sample) was used for  $(\text{NH}_4)_3\text{GeF}_7$ .

The low-temperature experiments were carried out using a closed cycle helium cryostat ARS CS204-X1.SS with LakeShore 340 temperature controller. The temperature was monitored by a calibrated silicon diode LakeShore DT-670SD1.4L. The thermal interface was indium foil. Measurements were taken inside the cryostat under pressure  $10^{-6}$  mBar. The above instrumentation allows to vary the sample cooling rate from 0.1 K/min up to 0.7 K/min with 0.1 K/min intervals. The experiments were carried out in the dynamic regime by varying the sample temperature and it was identical to the measurement procedure in our earlier work [13]. The uncertainty of the measured temperature for a given rate can be estimated as a difference between neighboring measurements. Overall time for taking a single spectrum was within 30 s.

## 3. Discussion and conclusion

To better understand spectral differences in structural phase transitions results of this research are presented as a comparison of spectra of studied crystals. Figure 1 shows Raman spectra of  $(\text{NH}_4)_3\text{SnF}_7$ ,  $(\text{NH}_4)_3\text{GeF}_7$ ,  $(\text{NH}_4)_3\text{TiF}_7$  at temperatures corresponding to different phases of these crystals.

Totally symmetric stretching vibrations  $\nu_1(\text{A}_{1g})$  of octahedral groups  $\text{MeF}_6$  in the high-temperature phase in the range of  $600 \pm 50\text{ cm}^{-1}$  are the most intensive [14]. Another less intensive peak present in the heptafluorides under study corresponds to vibration  $\nu_5(\text{F}_{2g})$ . The frequency of the peak predictably shifts depending on the ionic radius of the central atom: for Sn –  $246\text{ cm}^{-1}$ , for Ti –  $282\text{ cm}^{-1}$  and for Ge –  $325\text{ cm}^{-1}$ . Internal bending vibrations of  $\nu_2(\text{E}_g)$  types in  $\text{MeF}_6$  group are in the range of  $470\text{ cm}^{-1}$ . Low intensity in the titanium heptafluoride spectra denies their recording. The spectral line at  $67\text{ cm}^{-1}$  corresponds to the rotation of  $\text{MeF}_6$  octahedra. Analysis and comparison of spectral changes in the vibration region of  $\text{MeF}_6$  octahedra make possible to state: in  $(\text{NH}_4)_3\text{SnF}_7$  in accordance with structural and calorimetric data in the spectra at 360 K structural transformation takes place at which mode  $583\text{ cm}^{-1}$  splits into two peaks with frequencies  $586\text{ cm}^{-1}$ , corresponding to vibrations of  $(\text{Sn}2)\text{F}_6$ , and  $580\text{ cm}^{-1}$  –



**Figure 1.** Raman spectra of heptafluorides at different temperatures in the oscillation range of  $\text{MeF}_6$  polyhedra.

$(\text{Sn}_2)\text{F}_6$ , because of two octahedra in the structure of phase  $(Pa-3)$  [7]. In the region of  $160\text{ cm}^{-1}$   $\text{NH}_4$  exhibits rocking vibrations.

With further cooling to 8 K the bands shift, their intensities increase and the width of the spectral lines decreases. The broad band at  $246\text{ cm}^{-1}$  ( $\text{F}_{2g}$ ) of triply degenerate vibration below 150 K splits into modes with frequencies  $227$ ,  $246$ ,  $252\text{ cm}^{-1}$  and a mode at  $297\text{ cm}^{-1}$  emerges. Similar changes are observed with the band at  $67\text{--}87\text{ cm}^{-1}$ , it can be seen to consist of lines with maxima at  $70$ ,  $83$ ,  $90$ ,  $99$ ,  $110\text{ cm}^{-1}$  (Figure 1).

In  $(\text{NH}_4)_3\text{TiF}_7$  crystal two structural phase transitions take place at  $T_1 = 360\text{ K}$  and  $T_2 = 285\text{ K}$ , vividly manifesting in the spectra. During the first phase transition from  $P4/m\bar{3}m \rightarrow P4/mnc$  two fairly wide bands corresponding to vibrations of  $\text{TiF}_6$  can be observed. The vibration corresponding to rotation of  $\text{TiF}_6$  octahedra at frequency

$67\text{ cm}^{-1}$  disappears with increasing intensity of the Rayleigh wing. In the low-temperature phase  $Pa-3$  during the second phase transition below  $285\text{ K}$  in the region of  $600\text{ cm}^{-1}$ , like in  $(\text{NH}_4)_3\text{SnF}_7$  the line splits and two peaks emerge in the spectrum:  $614\text{ cm}^{-1}$  – corresponding to vibration of  $(\text{Ti}2)\text{F}_6$ , and  $606\text{ cm}^{-1}$  to  $(\text{Ti}1)\text{F}_6$  [9–12]. Translatory vibrations of ammonium are in the region of  $200\text{--}250\text{ cm}^{-1}$ , slightly below  $150\text{ cm}^{-1}$ , rocking vibrations of  $\text{NH}_4$  emerge. Emergence of the intensive peak in the spectra below the phase transition temperature in the region of  $97\text{ cm}^{-1}$  is connected with decreasing length of the bond between the free fluorine atom (F) and  $\text{NH}_4$  group. With further cooling to  $8\text{ K}$  the bands slightly shift, their intensities increase and the spectral linewidths decrease [12] (Figure 1).

$(\text{NH}_4)_3\text{GeF}_7$  has been found to have three successive structural transitions at temperatures  $T_1 = 279\text{ K}$ ,  $T_2 = 270\text{ K}$ ,  $T_3 = 229\text{ K}$  [8]. In the Raman spectra in the range of octahedral group vibrations at  $223\text{ K}$  changes take place connected with structural phase transition: mode  $625\text{ cm}^{-1}$  splits into two components; however, the behavior of this vibration differs from the related stannum and titanium heptafluorides. This mode in a jump splits at temperature  $223\text{ K}$ , without pre-transition changes; such a behavior is specific for this compound and indicates different nature and mechanism of the phase transition as compared to the other crystals of the group. Phase transformation at  $279\text{ K}$  and  $270\text{ K}$  corresponding to transition of the second order do not manifest in the Raman spectra. Further decrease of temperature gives rise to numerous narrow spectral lines (Figure 1), indicative of considerable modification of the structure.

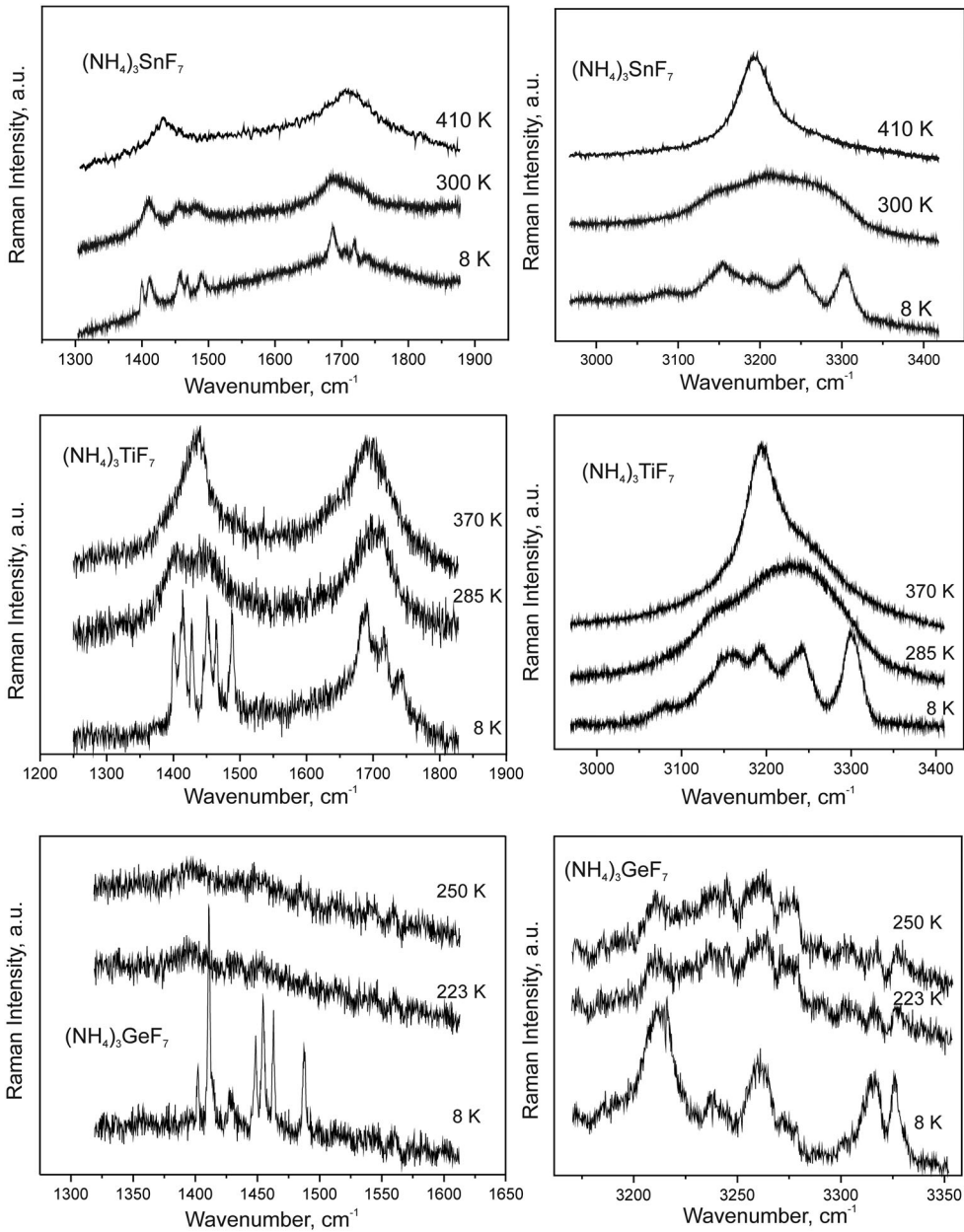
Figure 2 shows spectra in the region of vibration of tetrahedral ammonium ions of the crystals under study. In the spectrum of  $(\text{NH}_4)_3\text{SnF}_7$  at  $410\text{ K}$  above the phase transition the lines in the regions of the bending ( $1300\text{--}1800\text{ cm}^{-1}$ ) and stretching ( $3000\text{--}3350\text{ cm}^{-1}$ ) vibration of ammonium ions exhibit bigger half-width with maxima at  $1430, 1695, 3192\text{ cm}^{-1}$ . This forms grounds to suggest that in this phase there are at least two independent ammonium tetrahedra. When the temperature decreases to  $300\text{ K}$ , the number of lines increases and at  $8\text{ K}$  we can observe minimum five peaks in the region of stretching vibrations and 8 in the region of bending vibrations.

In the spectrum of  $(\text{NH}_4)_3\text{TiF}_7$  at  $370\text{ K}$ , above the second phase transition, the lines remain fairly wide, and at  $300\text{ K}$  there are two translationally independent  $\text{NH}_4$  tetrahedra within the unit cell. This forms grounds to suggest the presence of at least two independent tetrahedra in the high-temperature phase, too [12]. The spectral profile at  $8\text{ K}$  in the region of bending vibrations of  $\text{NH}_4$  can be described by at least ten peaks, and in the region of internal stretching vibrations of  $\text{NH}_4$  – by six peaks. Emergence of numerous lines in the spectrum at low temperatures in these two crystals is associated with decreasing local symmetry of  $\text{NH}_4$  tetrahedra.

Spectral changes of ammonium groups in  $(\text{NH}_4)_3\text{GeF}_7$  are unusual, but formation of hydrogen bonds can hardly be argued [8].

Thus, replacement of central atoms in the series of double fluoride salts  $(\text{NH}_4)_3\text{Me}^{4+}\text{F}_7$  ( $\text{Me}^{4+}$ : Sn, Ti, Ge) predictably not only changes the order of transitions, but causes structural disorder of different degree, which is one of main features of these fluorides crystallizing in the high-symmetry structures.

In  $(\text{NH}_4)_3\text{SnF}_7$ , one phase transition of ferroelastic nature takes place [7], and, in accordance with spectral data, it is associated with ordering of octahedral and



**Figure 2.** Raman spectra of heptafluorides under study at different temperatures in the region of internal vibrations of tetrahedral ammonium groups.

tetrahedral groups in the low-temperature triclinic phase. Two structural phase transitions realize in  $(\text{NH}_4)_3\text{TiF}_7$ , emergence of Rayleigh wing at 360 K forms grounds to suggest disordering of fluorine octahedra, the phase transition at 285 K, earlier defined as reconstructive,  $\text{TiF}_6$  octahedra get ordered, and numerous lines appear in the spectrum at low temperatures associated with decreasing local symmetry of  $\text{NH}_4$  octahedra. X-ray diffraction analysis showed that  $(\text{NH}_4)_3\text{GeF}_7$  undergoes a sequence of structural

phase transitions of the form  $P4/mbm-Pbam-P12_1/c1-Pa-3$ . The first two transitions are ferroelastic. The transition into the low-temperature cubic phase is defined as a reconstructive one of the first order [8]. However, in accordance with the spectral data in germanium-based fluorides, a pronounced phase transition takes place in this material at 223 K, associated with an ordering of octahedra that remains stable with further decrease of temperature. The changes taking place in the tetrahedral ammonium group can be described by gradual ordering.

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