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# Raman Scattering Study of Temperature Phase Transitions in $(\text{NH}_4)_3\text{MoO}_3\text{F}_3$

A. S. KRYLOV,<sup>1,\*</sup> S. N. KRYLOVA,<sup>1</sup> A. N. VTYURIN,<sup>1</sup>  
N. M. LAPTASH,<sup>2</sup> AND A. G. KOCHAROVA<sup>1</sup>

<sup>1</sup>Kirensky Institute of Physics SB RAS, 660036, Krasnoyarsk, Russia

<sup>2</sup>Institute of Chemistry FEB RAS, Vladivostok, 690022, Russia

*Raman scattering spectra of  $(\text{NH}_4)_3\text{MoO}_3\text{F}_3$  crystal have been studied in temperature range from 77 to 377 K. Parameters of Raman lines have been quantitatively analyzed. Transitional anomalies were found in the internal modes octahedral groups  $\text{MoO}_3\text{F}_3$  and ammonium groups at 297 K. The ferroelectric phase transition (297 K) in  $(\text{NH}_4)_3\text{MoO}_3\text{F}_3$  is associated with the partly ordering of octahedral  $\text{MoO}_3\text{F}_3$  and the ammonium cations. The ferroelastic phase transition (205 K) is associated with the further ordering of octahedral  $\text{MoO}_3\text{F}_3$ .*

**Keywords**  $(\text{NH}_4)_3\text{MoO}_3\text{F}_3$ ; temperature phase transitions; Raman scattering

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## 1. Introduction

$(\text{NH}_4)_3\text{MoO}_3\text{F}_3$  crystal belong to a large family of perovskite-like crystals. The crystalline, ceramic, and film materials with perovskite-like structures are widely used as functional elements due to their remarkable properties: ferroelectricity, ferromagnetism and ferroelasticity [1, 2]. Infrared spectra oxyfluoride complexes  $\text{TiOF}_5^{3-}$ ,  $\text{VOF}_5^{3-}$ ,  $\text{NbO}_2\text{F}_4^{3-}$ ,  $\text{MoO}_3\text{F}_3^-$  and  $\text{WO}_3\text{F}_3^-$  were investigated Von K. Dehnicke, G. Pausewang *et al.* [3, 4]. Temperature phase transitions in isostructural oxyfluorides were investigated by using calorimetric method, x-ray diffraction and vibrational spectroscopy [5–9].

$(\text{NH}_4)_3\text{MoO}_3\text{F}_3$  crystal has cubic structure at room temperature (space group  $Fm\bar{3}m$ ,  $Z = 4$ ) Mo is located in position 4 (a), N in 4 (b) and 8 (c) positions, O and F atoms are randomly distributed in two independent positions [24(e) and 96(j)]. The slightly compressed  $\text{MoX}_6$  ( $X = \text{O}, \text{F}$ ) octahedron has a *fac* configuration with the central atom shifted toward the face occupied by three O atoms [10]. The tetrahedral cation in the 4b position of the  $Fm\bar{3}m$  structure must be disordered in at least two positions [11]. The  $(\text{NH}_4)_3\text{MoO}_3\text{F}_3$  crystal undergoes ferroelectric and ferroelastic structural phase transitions at temperatures of  $T_1 = 297$  and  $T_2 = 205$  K, respectively [12]. Significant temperature hysteresis ( $\delta T_1 \approx 13$  K) suggests that the transition from cubic phase is a first-order transformation. The structures of low-temperature phases not determined since the crystals

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\*Corresponding author. E-mail: slanky@iph.krasn.ru

changed into their polydomain state. The symmetry of distorted phase (at  $T < 205$  K) in  $(\text{NH}_4)_3\text{MoO}_3\text{F}_3$  crystals is not higher than monoclinic [12].

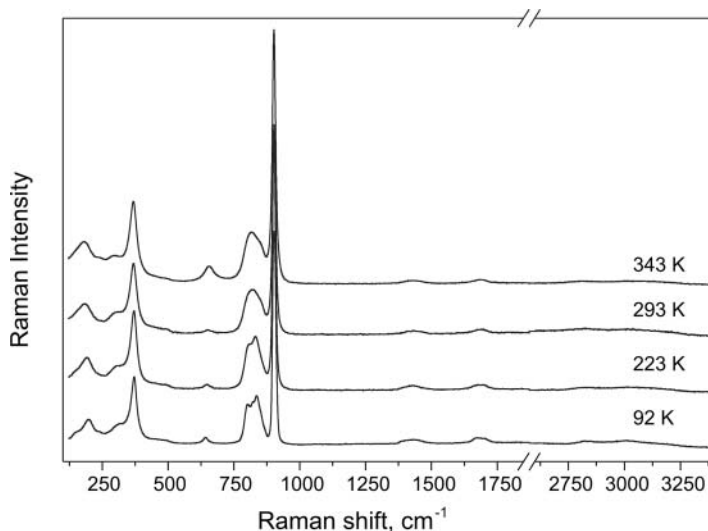
Phase transitions in  $(\text{NH}_4)_3\text{MoO}_3\text{F}_3$  can be governed by the ordering of  $\text{MoO}_3\text{F}_3$  octahedra,  $\text{NH}_4$  groups. To define role molecular groups in the mechanism of phase transitions we have performed Raman scattering study of temperature phase transitions.

## Experimental Technique and Results

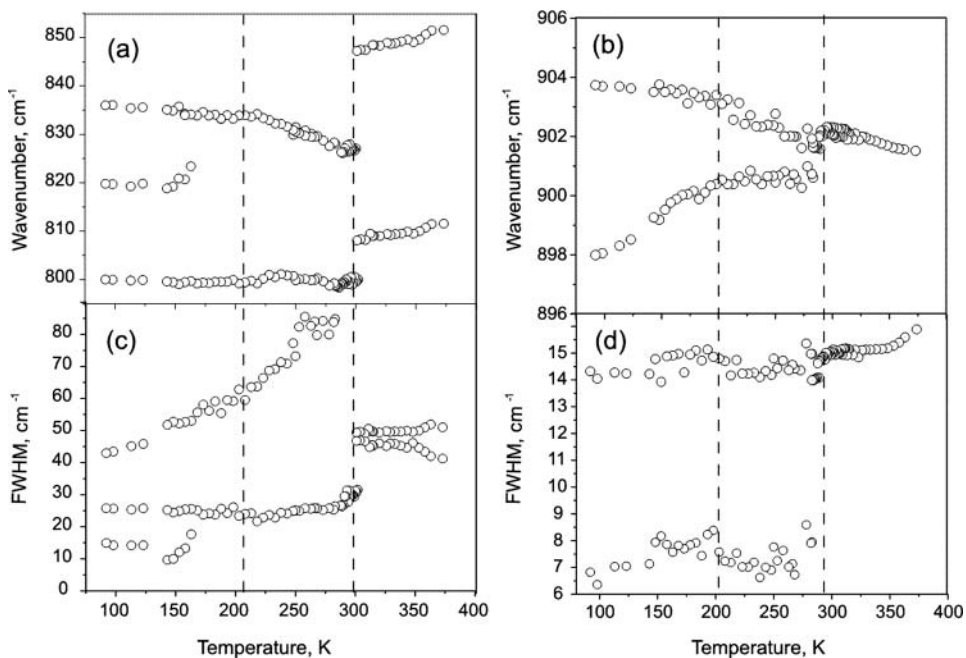
Raman spectra in the backscattering geometry were produced with Fourier-Raman spectrometer RFS 100/S (Bruker) for  $70\text{--}3500\text{ cm}^{-1}$  range with resolution  $2\text{ cm}^{-1}$ . The  $1.06\text{ }\mu\text{m}$  Nd: YAG laser with power  $350\text{ mV}$  was used as source. Unoriented microcrystals were placed in a quartz-covered steel container. Temperature measurements were made with Specac optical cryostat, making possible to obtain spectra in temperature range  $77\text{--}370\text{ K}$ , stabilization accuracy  $\pm 0.1\text{ K}$  [9, 10]. To produce quantitative information about spectral line parameters their profiles were deconvoluted employing the Lorentz profile [13].

Experimental Raman spectra transformation with temperature is shown on Fig. 1. The spectrum can be divided into several regions: medium-wavenumber region of internal vibrations  $\text{MoO}_3\text{F}_3^-$  ions –  $77\text{--}1000\text{ cm}^{-1}$ , high-wavenumber from  $1300$  to  $2000\text{ cm}^{-1}$  region contains bending modes of the ammonium ions and from  $2500$  to  $3500\text{ cm}^{-1}$  region contains lines of the stretching of the ammonium ions.

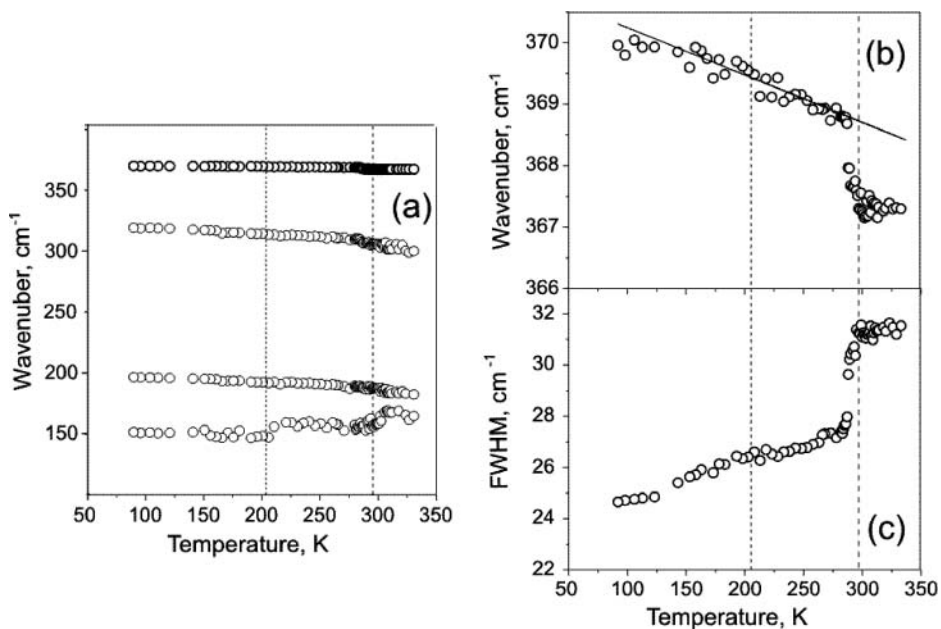
The main changes take place in the region of stretching modes of  $\text{Mo} - \text{O}$  bond, i. e. in the region of  $750\text{--}910\text{ cm}^{-1}$ . Quantum chemical simulations for isostructural  $\text{WO}_3\text{F}_3^{3-}$  ions were performed by Vtyurin *et al.* [9]. The simulation showed the region  $800\text{--}1000\text{ cm}^{-1}$  corresponding to stretching vibrations  $\text{W} - \text{O}$  of the  $\text{WO}_3\text{F}_3^{3-}$  ions. We believe the most intensive line ( $901\text{ cm}^{-1}$ ) of the Raman spectrum  $(\text{NH}_4)_3\text{MoO}_3\text{F}_3$  crystal corresponds to the totally symmetrical stretching vibrations of the  $\text{Mo} - \text{O}$  bonds of  $[\text{MoO}_3\text{F}_3]^{3-}$  ions. At temperature  $370\text{ K}$  the profile consists of three lines:  $810\text{ cm}^{-1}$ ,  $850\text{ cm}^{-1}$  and  $901\text{ cm}^{-1}$ . Dependence of the bands components' positions  $810\text{ cm}^{-1}$ ,  $850\text{ cm}^{-1}$  with temperature reviewed by Fig. 2(a),  $901\text{ cm}^{-1}$  reviewed by Fig. 2(b). New line emerges below  $297\text{ K}$  in  $900\text{ cm}^{-1}$



**Figure 1.** Raman spectra transformation vs. temperature.



**Figure 2.** Dependence of the bands components' positions 810 cm<sup>-1</sup>, 850 cm<sup>-1</sup> vs. temperature – (a), 901 cm<sup>-1</sup> – (b). Full widths at half-maximum vs. temperature for line 810 cm<sup>-1</sup>, 850 cm<sup>-1</sup> – (c), 901 cm<sup>-1</sup> – (d).



**Figure 3.** Dependence of the bands components' positions 170 cm<sup>-1</sup>, 190 cm<sup>-1</sup>, 310 cm<sup>-1</sup>, 367 cm<sup>-1</sup> vs. temperature – (a). The wavenumber for line 320 cm<sup>-1</sup> – (b). Full widths at half-maximum dependences from temperature – (c).

region a (Fig. 2(b)). New line emerges below 205 K about  $830\text{ cm}^{-1}$  (Fig. 2(a)). Positions of lines  $810\text{ cm}^{-1}$ ,  $850\text{ cm}^{-1}$  shifts to  $800\text{ cm}^{-1}$ ,  $825\text{ cm}^{-1}$  correspondingly (at 297 K). Dependence of linewidths (full widths at half-maximum) vs. temperature is shown on Fig. 2(c) for line  $810\text{ cm}^{-1}$ ,  $850\text{ cm}^{-1}$ , on Fig. 2(d). The linewidths changed significantly at  $T_1 = 297\text{ K}$  (Fig. 2(c)). These changes in the spectra are associated with first order phase transition.

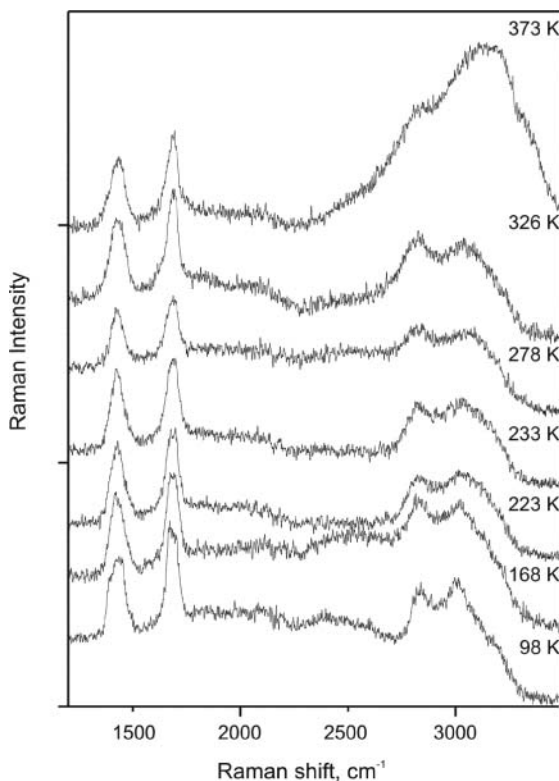
Medium-wavenumber region contains stretching vibrations Mo – F and bending modes of  $\text{MoO}_3\text{F}_3^-$  ions. Dependence of the bands components' positions  $170\text{ cm}^{-1}$ ,  $190\text{ cm}^{-1}$ ,  $310\text{ cm}^{-1}$ ,  $367\text{ cm}^{-1}$  with temperature reviewed by Fig. 3(a).

The position and full width on half maximum dependences from temperature for line  $367\text{ cm}^{-1}$  ( $\text{MoF}_3$  vibrations) is shown on Fig. 3(b, c). The wavenumber and width growth rate changes at 297 K. Extrapolation of the position dependence in the second phase (from 205 K to 297 K) (solid curve) with the function [14]:

$$\Omega(T) = \Omega_0 + A\left(\left(1 + \frac{1}{\exp(\hbar\Omega_1/(k_B T))} - 1\right) + \frac{1}{\exp(\hbar\Omega_2/(k_B T))} - 1\right), \Omega_1 + \Omega_2 = \Omega_0 \quad (1)$$

is given in Fig. 3(b).  $\hbar$  – reduced Planck's constant,  $k_B$  – Boltzmann constant. The Eq. (1) specifies the contributions of three-phonon processes to the frequency shift. Extrapolated to  $T = 0$  wavenumber equals  $371\text{ cm}^{-1}$ .  $A = -0.161\text{ cm}^{-1}$ ,  $\Omega_1 \approx 213\text{ cm}^{-1}$ , and  $\Omega_2 \approx 158\text{ cm}^{-1}$ .

The transformation Raman spectra with temperature for ammonium group vibrations reviewed on Fig. 4. The lines positions are close to the positions of internal modes of the



**Figure 4.** Raman spectra transformation of ammonium groups vs. temperature.

free ion respectively [15]. In the Raman spectra in 1200 to 3500  $\text{cm}^{-1}$  region some changes occur.

The positions of lines changes at temperature  $T_1$ . The widths decrease with temperature decrease. Infrared spectroscopy investigation of  $(\text{NH}_4)_3\text{MoO}_3\text{F}_3$  demonstrated that  $\text{NH}_4^+$  groups order and distort by the crystal environment [16]. Raman spectra changes vs. temperature indicating that the ordering of  $\text{NH}_4^+$  groups.

## Conclusion

Obtained and analyzed Raman spectra of  $(\text{NH}_4)_3\text{MoO}_3\text{F}_3$  polycrystalline or of small un-oriented crystals at different temperatures in range from 77 to 377 K.

The cubic phase are disordered orientationally, this is evidenced by wide internal lines away from the transition point. Phase transitions sequence in temperature decrease agrees with calorimetric measurement data. The most intense line ( $901 \text{ cm}^{-1}$ ) of the Raman spectrum corresponds to the totally symmetric stretching vibrations of the Mo–O bonds of  $[\text{MoO}_3\text{F}_3]^{3-}$  ions. Cooling of the crystal below the phase transitions temperature (297 and 205 K) gives rise to orientational ordering of the  $[\text{MoO}_3\text{F}_3]^{3-}$  ions. This manifests itself in a sharp narrowing of the lines corresponding to the vibrations of the Mo–O bonds. The phase transition at 297 K is associated with the ordering of the ammonium cations.

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