

LATTICE DYNAMICS
AND PHASE TRANSITIONS

A Raman Scattering Study of the Phase Transition
in the $(\text{NH}_4)_3\text{WO}_3\text{F}_3$ Oxyfluoride

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Abstract—The Raman scattering spectra of polycrystalline samples of the $(\text{NH}_4)_3\text{WO}_3\text{F}_3$ perovskite-like oxyfluoride were measured at frequencies of 70–3600 cm^{-1} in the temperature range 93–323 K, including the transition from the orientationally disordered cubic phase to the low-symmetry phase. Transitional anomalies in the spectral parameters were revealed in the frequency ranges of internal vibrations of the ammonium ions and WO_3F_3 octahedral groups. An analysis of the experimental results allowed the conclusion that the phase transition under study is associated primarily with the ordering of the octahedral groups.

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1. INTRODUCTION

Perovskite-like fluorides of the general formula A_3BX_6 (where A and B are metal cations and X is a halogen or oxygen anion) in the high-temperature phase have cubic symmetry (space group $Fm\bar{3}m$, $Z = 4$) and belong to the cryolite–elpasolite family [1]. As was shown earlier by von Pausewang and Rüdorff [2], the cubic symmetry of the high-temperature phase is retained in crystals of mixed composition $A_3\text{BO}_x\text{Hal}_{6-x}$ (where Hal is a halogen ion and x depends on the valence states of the A and B ions), in which the halogen and oxygen atoms are randomly distributed over the crystal lattice and the local symmetry of the $\text{BO}_x\text{Hal}_{6-x}$ octahedral ion is lower than cubic [3, 4] (the structure of the cubic phase is shown in Fig. 1).

As the temperature decreases, oxyfluorides and fluorides of this family undergo sequences of phase transitions, which can be associated with the orientational ordering of the octahedral ions [1, 5, 6]. The distorted phases in this case can be different in nature. Specifically, these phases are ferroelastic in the fluoride systems and can be either ferroelastic or ferroelectric in the oxyfluoride systems.

The substitution of the ammonium ion for the A^+ cation can result in an additional structural disorder associated with the orientational degrees of freedom of this ion. Moreover, one of these cation positions in the cubic structure, namely, $\text{NH}_4(\text{I})$, has the local symmetry

O_h and the tetrahedral ion occupying this position should be orientationally disordered.

We are witnessing only the beginning of studies of phase transitions in ammonium oxyfluorides [6]. The present publication reports on the results of a Raman spectroscopic study of the phase transition in crystals of ammonium oxyfluoride $(\text{NH}_4)_3\text{WO}_3\text{F}_3$.

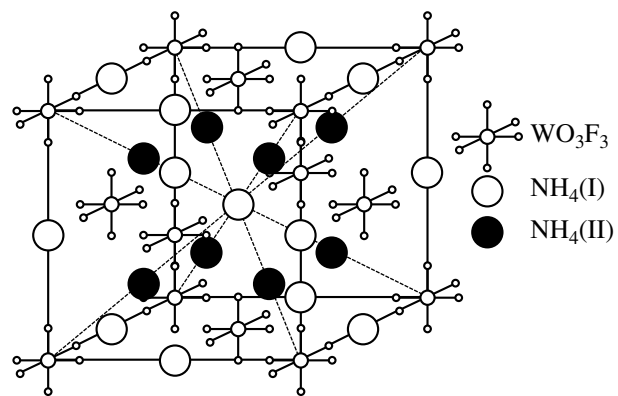


Fig. 1. Structure of the unit cell in the cubic phase of the $(\text{NH}_4)_3\text{WO}_3\text{F}_3$ crystal. Large-sized open and closed circles stand for orientationally disordered ammonium cations. $\text{NH}_4(\text{I})$ is an ammonium ion in the position with the local symmetry O_h , and $\text{NH}_4(\text{II})$ is an ammonium ion in the position with the local symmetry T_d . The positions of oxygen and fluorine atoms in the WO_3F_3 octahedra are likewise unknown.

2. SAMPLE PREPARATION AND EXPERIMENTAL TECHNIQUES

Ammonium oxyfluoride $(\text{NH}_4)_3\text{WO}_3\text{F}_3$ was prepared from a hot solution of $(\text{NH}_4)_2\text{WO}_2\text{F}_4$ with an excess of NH_4F , followed by the addition of a NH_4OH solution. This procedure resulted in the precipitation of small, transparent, colorless octahedral crystals. Further crystallization through slow evaporation in air yielded octahedral single crystals with an edge of approximately $40\ \mu\text{m}$. For more details of the synthesis procedure, the reader is referred to [6]. X-ray diffraction analysis revealed that the crystals have a cubic structure with a unit cell parameter of $0.9156\ \text{nm}$ (space group $Fm\bar{3}m$); no peaks attributed to impurities of the initial components or foreign phases were observed in the x-ray diffraction patterns.

The Raman scattering spectra were recorded on a Bruker RFS100/S Fourier-transform Raman spectrometer in the frequency range $70\text{--}3600\ \text{cm}^{-1}$ in the back-scattering geometry with a resolution of $1\ \text{cm}^{-1}$. The spectra were excited by radiation from a Nd : YAG laser operating at a wavelength of $1.06\ \mu\text{m}$ with a power of $350\ \text{mW}$. Microcrystals of the compound under study were placed in a metallic container covered with silica glass. For the recording of the spectra under changes in temperature, the container was mounted inside a Specac cryostat permitting spectral measurements in the range of $83\text{--}523\ \text{K}$ with the temperature stabilized to within $\pm 0.1\ \text{K}$.

Quantitative information on the parameters of the spectral lines was obtained by processing the experimental data with the PeakFit and SigmaPlot 8.0 software packages (SPSS Inc.) using the Voigt and dispersion profiles for the corresponding lines (after the inclusion of the Bose–Einstein temperature factor accounting for the population of the vibrational levels).

3. EXPERIMENTAL RESULTS AND THEIR DISCUSSION

3.1. The General Structure of the Raman Spectrum

Figure 2 shows the experimental Raman spectrum of the $(\text{NH}_4)_3\text{WO}_3\text{F}_3$ crystal at room temperature. As is clearly seen, this spectrum can be divided into four ranges.

In the ranges $2700\text{--}3500$ and $1200\text{--}1600\ \text{cm}^{-1}$, the Raman spectrum contains two lines, each attributed to the stretching and bending internal modes of the ammonium ions. Although these lines are fairly broadened, they are not split and their frequencies (2770 and $3092\ \text{cm}^{-1}$ for the stretching vibrations and 1489 and $1697\ \text{cm}^{-1}$ for the bending vibrations) are very close to those of the internal modes of the free ion (3040 , 3145 , and 1400 , $1680\ \text{cm}^{-1}$, respectively [7]). Since the shift in the above frequencies is relatively small and no positional splitting or splitting associated with the removal

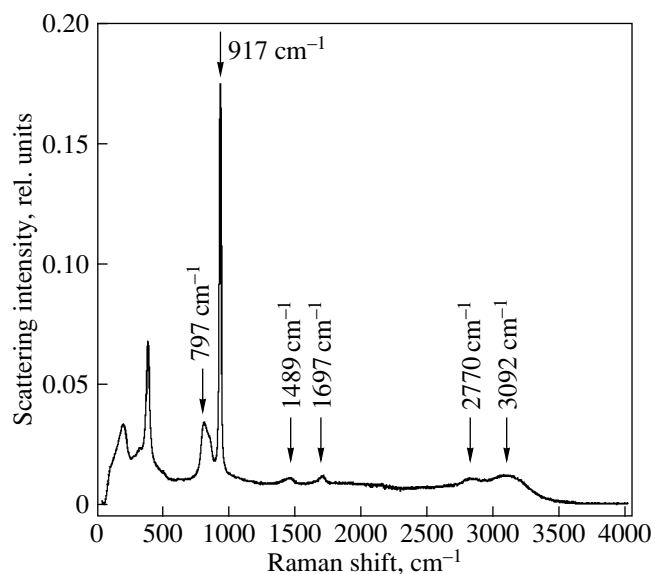


Fig. 2. Total Raman spectrum of the $(\text{NH}_4)_3\text{WO}_3\text{F}_3$ crystal at room temperature.

of the degeneracy of the F and E modes occurs, the ammonium ions are only slightly distorted by the crystal environment and weakly interact with each other.

In the range $750\text{--}1000\ \text{cm}^{-1}$, the Raman spectrum contains lines assigned to the stretching vibrations of the $\text{W}\text{--}\text{O}$ bonds in the $\text{WO}_3\text{F}_3^{3-}$ ions. In order to interpret these lines, we performed quantum-chemical calculations for two possible configurations of the $\text{WO}_3\text{F}_3^{3-}$ ions with symmetries C_{3v} (*cis*- $[\text{WO}_3\text{F}_3]^{3-}$) and C_{2v} (*trans*- $[\text{WO}_3\text{F}_3]^{3-}$). The calculations were carried out at the restricted Hartree–Fock level with the use of the B3LYP density functional in the SBKJC valence basis set [8] in combination with a pseudorelativistic core potential complemented by two diffuse functions for the W, F, and O atoms. All computations were run on a 16-processor Linux cluster (the MBC1000 system) with the GAMESS program package [9]. Since the optimization of the geometric parameters of the highly charged anions $[\text{WO}_3\text{F}_3]^{3-}$ in terms of mechanical stability led to overestimated interatomic distances as compared to experimental data [6] and to a noticeable shift in the vibrational frequencies, we calculated the optimum geometric parameters of the $[\text{Na}_6\text{WO}_3\text{F}_3]^{3-}$ cluster. The geometric parameters thus obtained were used in subsequent calculations. A more detailed description of the technique employed can be found in [10]. The vibrational frequencies and relative intensities of the Raman lines for the two configurations of the $\text{WO}_3\text{F}_3^{3-}$ ions are listed in the table.

The frequency of the most intense line ($917\ \text{cm}^{-1}$) in the experimental Raman spectrum at room temperature nearly coincides with the calculated frequency

Results of the quantum-chemical (ECP/SBKJC/B3LYP) calculation of the vibrational spectrum of the $\text{WO}_3\text{F}_3^{3-}$ ions

Symmetry of the vibrational mode	Frequency, cm^{-1}	Relative intensity of the Raman line
<i>cis</i> configuration, C_{3v}		
A_1	915	37.1
E	821	4.7
A_1	415	3.7
E	342	0.3
A_1	336	0.3
E	334	1.7
A_1	274	0.3
E	252	0.2
E	175	0.3
A_2	137	0.0
<i>trans</i> configuration, C_{2v}		
A_1	887	12.4
A_1	810	13.6
B_1	745	0.5
A_1	455	4.9
B_2	433	0.0
B_1	358	0.7
A_1	328	1.1
A_2	292	0.0
B_1	308	1.1
A_1	263	3.9
B_2	256	0.8
B_2	229	0.4
B_1	211	0.6
A_1	151	2.6
B_2	0.35	0.0

(915 cm^{-1}) of the totally symmetric stretching vibrations of the W–O bond for the *cis* configuration of the $\text{WO}_3\text{F}_3^{3-}$ ion. The frequency of the complex band observed in the range 775–850 cm^{-1} is close to the frequency of the doubly degenerate asymmetric stretching vibrations of the $\text{WO}_3\text{F}_3^{3-}$ ion in the same configuration (the calculated frequency is 821 cm^{-1}). The calculated frequency (810 cm^{-1}) of the strongest stretching vibration of the W–O bond for the *trans* configuration of the $\text{WO}_3\text{F}_3^{3-}$ ion also falls in the aforementioned range. Attempts to deconvolute this band into its constituent parts with the use of the dispersion or Voigt profiles (Fig. 3) showed that it is a superposition of at least three single lines located at 784, 814, and 845 cm^{-1} . This triplet apparently involves two lines formed as a result of

lifting the degeneracy of the E vibrations of the $\text{WO}_3\text{F}_3^{3-}$ ion in the *cis* configuration and an intense line attributed to the A_1 vibrations of this ion in the *trans* configuration (see table).

According to our calculations, a less intense but Raman-active line corresponding to the W–O stretching vibrations for the *trans* configuration of the $\text{WO}_3\text{F}_3^{3-}$ ion should lie at a frequency of 887 cm^{-1} . One does indeed observe here an increase in the spectral signal (Fig. 4), but it is too weak to warrant treating it as a spectral line.

The lines observed in the frequency range below 500 cm^{-1} are assigned to the stretching vibrations of the W–F bonds and to the bending vibrations of the

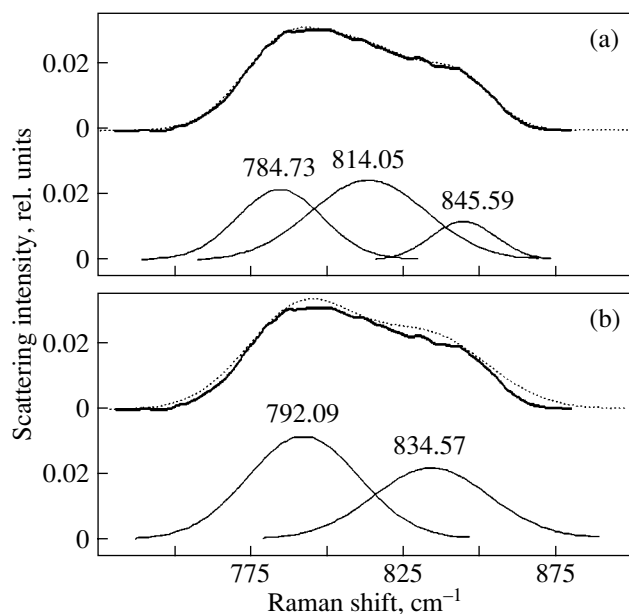


Fig. 3. Deconvolution of the spectral line observed in the range 775–850 cm^{-1} at $T = 232$ K into (a) three and (b) two components. Heavy lines are the experimental spectra, and dotted lines represent the sum of their constituent components. The spectral components shown by solid lines at the bottom of the panels have the following parameters (position/half-width expressed in inverse centimeters): 784.73/16.74–814.05/22.69–845.59/12.80 for three peaks and 792.09/21.62–834.57/22.70 for two peaks.

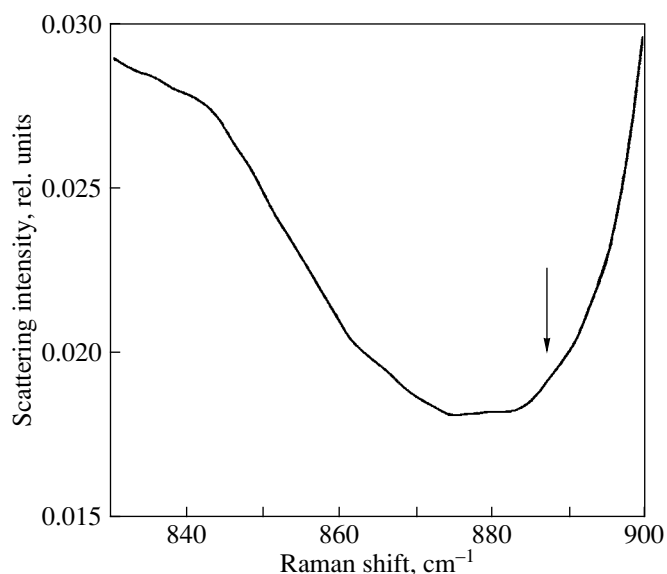


Fig. 4. Fragment of the Raman spectrum in the range of 880 cm^{-1} on an enlarged scale. The arrow indicates the calculated position of the W–O stretching vibration of the $\text{WO}_3\text{F}_3^{3-}$ ion in the *trans* configuration.

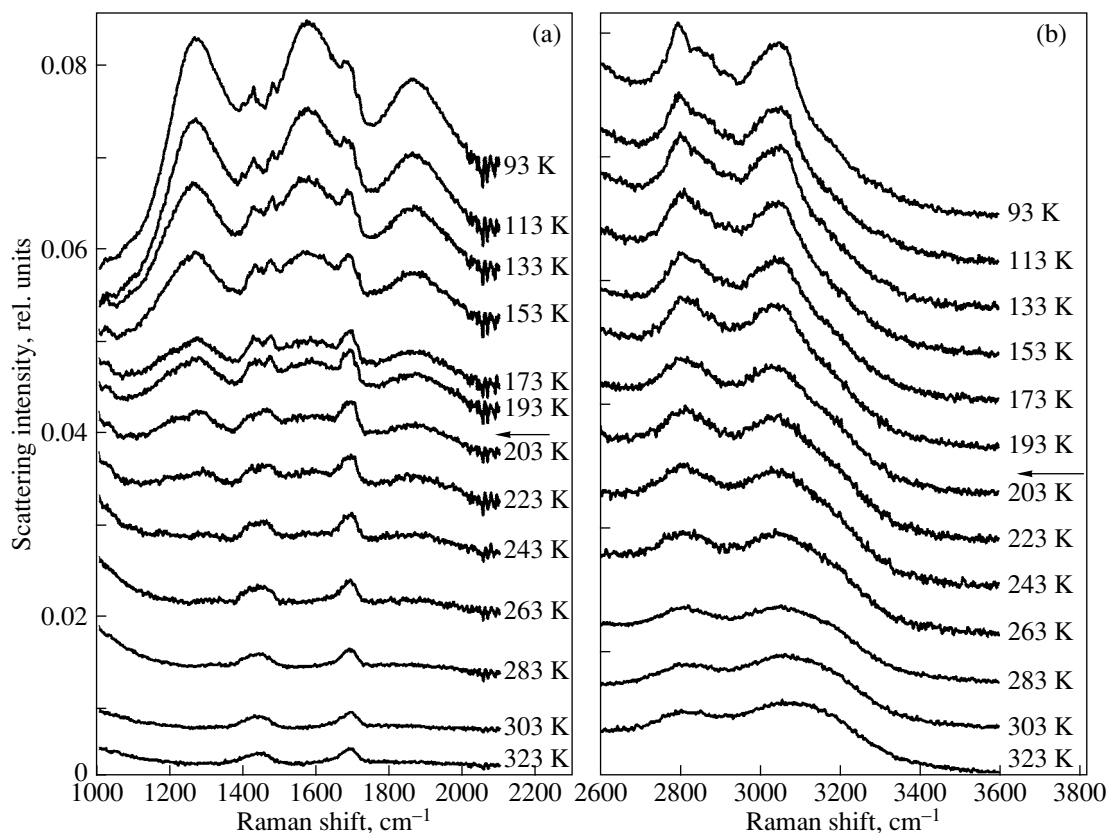


Fig. 5. Evolution of the Raman spectra of the (a) bending and (b) stretching internal vibrations of the ammonium ions during cooling. Arrows indicate the phase transition temperature.

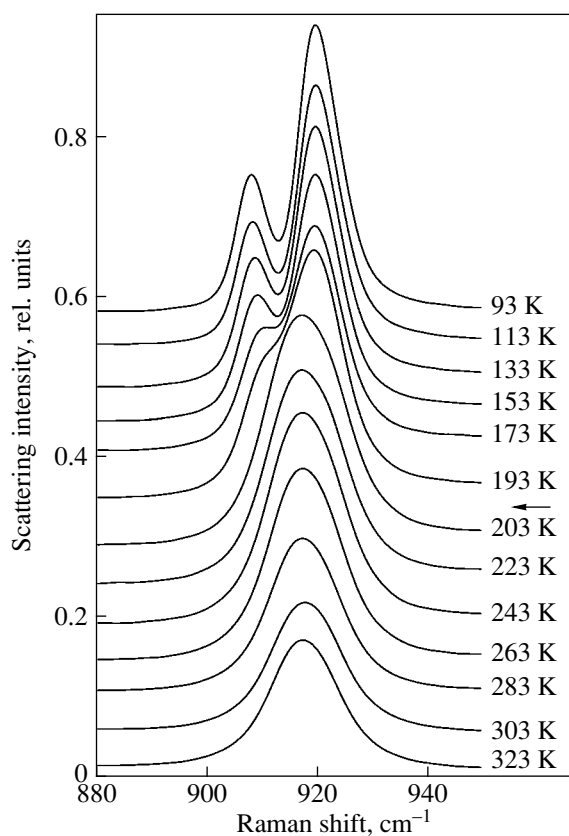


Fig. 6. Evolution of the spectral line at 917 cm^{-1} during the phase transition.

$\text{WO}_3\text{F}_3^{3-}$ ions. One likewise observes here good agreement between the experimental data and the calculation [10] performed for the C_{3v} conformer. Therefore, we can conclude that the $\text{WO}_3\text{F}_3^{3-}$ ions in the crystal under study reside predominantly in the *cis* configuration but are subject to intrasphere dynamics.

3.2. Temperature-Induced Transformation of the Raman Spectrum

The spectra measured during cooling of the sample to 200 K change only slightly (except for the expected small narrowing of the lines). Below 200 K (at the phase transition observed earlier in studies of x-ray diffraction and heat capacity [6]), the spectrum undergoes a substantial transformation.

In the range of stretching and bending internal vibrations of the ammonium ions, the scattering intensity increases significantly (Fig. 5) and complex structured bands appear in place of the single lines. As the temperature of the samples decreases to 90 K, the scattering intensity continues to increase and the bands remain broadened (the characteristic half-widths exceed 100 cm^{-1}).

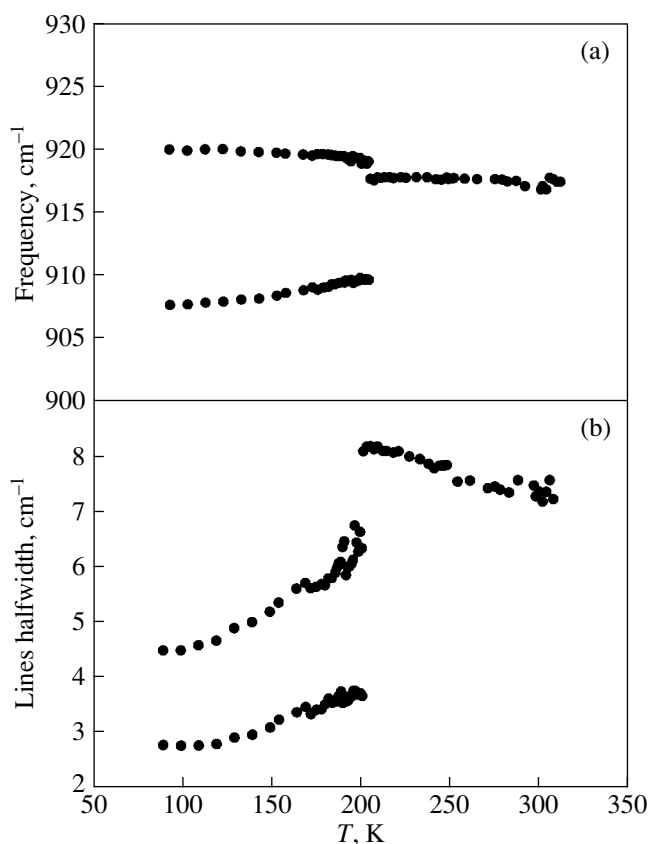


Fig. 7. Temperature dependences of (a) the frequency and (b) the half-width of the spectral line at 917 cm^{-1} .

The spectral lines attributed to the W–O stretching vibrations also change considerably. Below the phase transition temperature, the most intense line at 917 cm^{-1} is drastically narrowed and is split into two lines (Fig. 6). Figure 7 shows the temperature dependences of the frequency and half-width of the newly formed doublet. These dependences clearly illustrate the anomalous behavior of the decay of the two lines in the phase transition range. At the same time, the magnitude of the decay far from the phase transition temperature remains almost unchanged (in contrast, for instance, with the behavior of the linewidth corresponding to internal vibrations of the ordered elpasolite Rb_2KScF_6 [11]), which suggests that, in this particular case, the lifetime of these phonons is determined by their interaction with the disordered lattice rather than by the phonon–phonon interaction.

Similar changes occur with the spectral band located in the range $775\text{--}850\text{ cm}^{-1}$ (Fig. 8). Already 1–2 K below the phase transition temperature, its constituent lines substantially narrow and it becomes clearly visible that this band indeed consists of three lines. As the temperature decreases still more, each of them transforms into a doublet whose components become

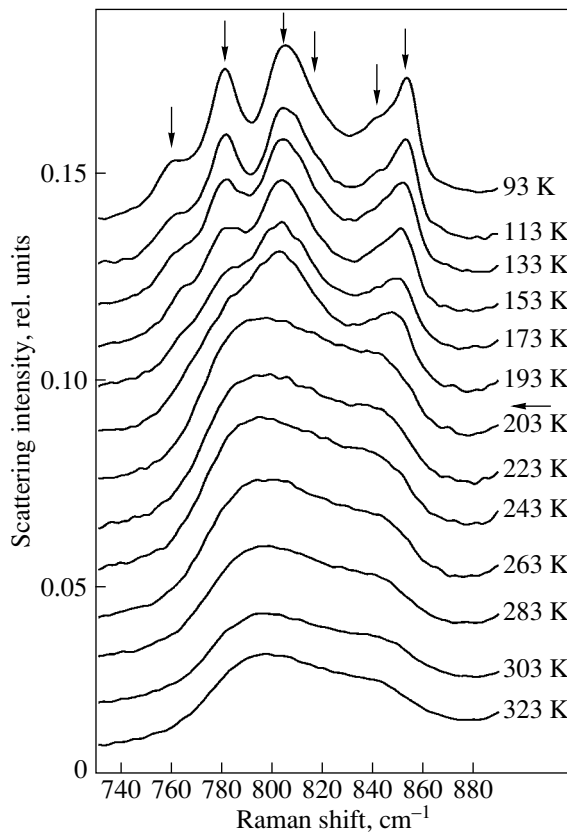


Fig. 8. Evolution of the Raman spectrum in the range 775–850 cm^{-1} during cooling. Vertical arrows indicate the positions of the spectral lines below the phase transition temperature.

more and more split apart in frequency (Fig. 9) and narrow insignificantly.

Similar changes, though not as pronounced, occur in the low-frequency range of the spectrum (Fig. 10).

It is obvious that the observed changes in the Raman spectrum are associated with the orientational ordering of the molecular ions upon the phase transition. As was already mentioned, both the ammonium and $\text{WO}_3\text{F}_3^{3-}$ ions are orientationally disordered in the cubic phase. The abrupt decrease in the linewidth corresponding to the W–O internal vibrations convincingly argues for the onset of orientational anion ordering below the phase transition temperature. However, the ammonium cations remain orientationally disordered. This accounts for the persisting large linewidths relevant to their internal vibrations. An enhanced interaction of the cations with the ordered anion sublattice brings about their noticeable distortion (it is conceivable that hydrogen bonds can arise between the ammonium protons and oxygen atoms of the ordered anion sublattice). As a result, the high-frequency part of the spectrum becomes more complex and the scattering intensity increases.

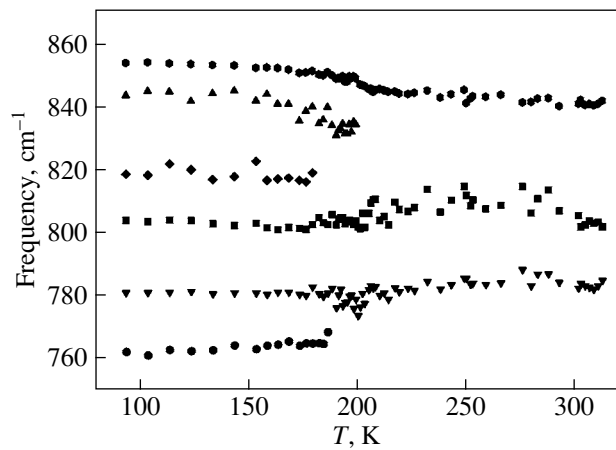


Fig. 9. Temperature dependences of the frequencies of the spectral lines in the range 775–850 cm^{-1} .

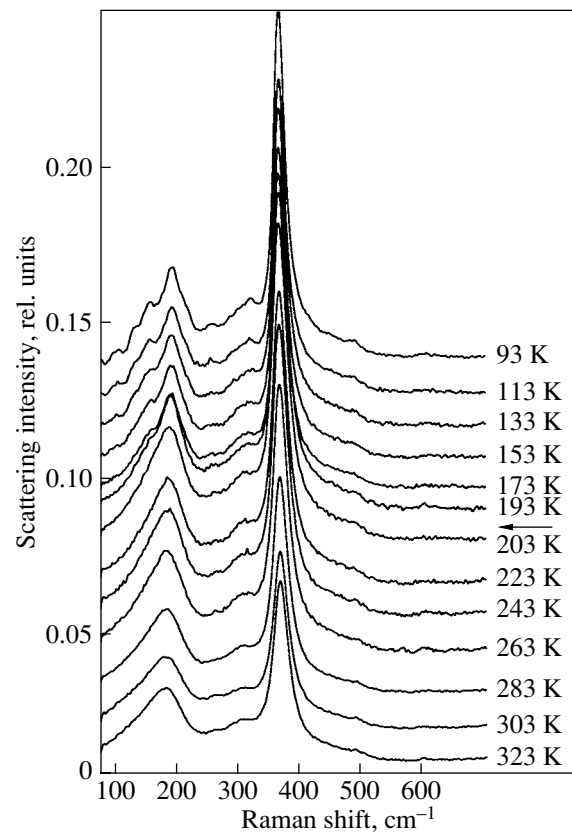


Fig. 10. Evolution of the Raman spectrum at low frequencies during cooling.

4. CONCLUSIONS

Thus, we measured and analyzed the total Raman scattering spectrum of the $(\text{NH}_4)_3\text{WO}_3\text{F}_3$ crystal in the temperature range 93–323 K and identified the lines of the stretching and bending internal vibrations of the

ammonium ions, as well as the vibrations of the W–O bonds in the $\text{WO}_3\text{F}_3^{3-}$ anions.

A comparison of the measured spectra of the stretching vibrations of the $\text{WO}_3\text{F}_3^{3-}$ anions with the results of the quantum-chemical calculations supported the conclusion that these ions in the structure of the crystal under study are present primarily in the *cis* configuration.

All molecular ions in the cubic phase of the crystal are orientationally disordered, which is confirmed by the large widths of the corresponding lines and by the weak temperature dependence of these widths far away from the phase transition point.

Cooling of the crystal below the phase transition temperature (200 K) gives rise to orientational ordering of the anion sublattice. This manifests itself in a sharp narrowing of the lines corresponding to the vibrations of the W–O bonds. The enhanced interaction of the ammonium cations with the ordering anion sublattice brings about their distortion, which results in the splitting of the lines attributed to their internal vibrations and in an increase in their intensity; however, the ammonium cations remain orientationally disordered.

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