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## PHASE TRANSITIONS, CRITICAL PHENOMENA, AND THE STRUCTURE AND DYNAMICS OF CRYSTAL LATTICES

# Raman Spectroscopic Study of the Phase Transitions in the $(NH_4)_3WO_3F_3$ Oxyfluoride

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**Abstract**—The Raman spectra of $(NH_4)_3WO_3F_3$ perovskite-like oxyfluorides are measured in the frequency range 70–3600 $cm^{-1}$. The anomalies observed in the spectral parameters upon phase transitions at a temperature of 200 K under atmospheric pressure and at room temperature under a pressure of 1.4 GPa are interpreted.

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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 a cubic elpasolite structure (space group $Fm\bar{3}m$, $Z = 4$) [1]. Upon partial substitution of oxygen ions for fluorine ions in the $A_3BO_xF_{6-x}$ compounds, the initial cubic symmetry is retained and the fluorine and oxygen ions are randomly distributed over the crystal lattice [2]. The substitution of ammonium ions for $A^+$ ions can lead to an additional structural disorder, because one of the cation positions in the cubic lattice has the local symmetry $O_h$ and the tetrahedral ammonium ion occupying this position must necessarily be disordered. As the temperature decreases, oxyfluorides of this family undergo sequences of phase transitions, which can be associated with the orientational ordering of the molecular ions [1, 3, 4]. The present paper reports on the results of the Raman spectroscopic study of these phase transitions in $(NH_4)_3WO_3F_3$ crystals.

## 2. RESULTS AND DISCUSSION

Figure 1 shows the experimental Raman spectrum of the $(NH_4)_3WO_3F_3$ crystal at room temperature. The spectrum was excited by radiation from a Nd : YAG laser (1.06 μm, 350 mW) and recorded on a Bruker RFS100/S Fourier-transform Raman spectrometer with a resolution of 1 $cm^{-1}$.

The Raman spectrum contains two lines in the frequency range 2700–3500 $cm^{-1}$ and two lines in the range 1200–1600 $cm^{-1}$. These lines are assigned to the stretching and bending internal vibrations of the ammonium ions, respectively. The lines are considerably broadened but are not split. The frequencies of the lines are very close to those of the internal modes of the free ion [5]. This indicates that the ammonium ions are only slightly distorted by the crystal environment and weakly interact with each other.

Below the phase transition temperature (200 K [4]), the scattering intensity increases significantly (Fig. 2) and complex structured lines appear in place of the single lines. As the temperature decreases to 90 K, the scattering intensity increases and the lines remain broadened.

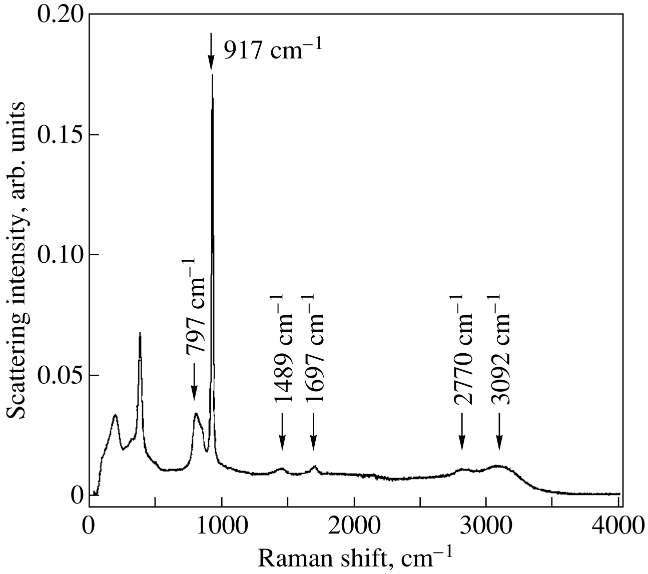

**Fig. 1.** Raman spectrum of the $(NH_4)_3WO_3F_3$ oxyfluoride at room temperature.

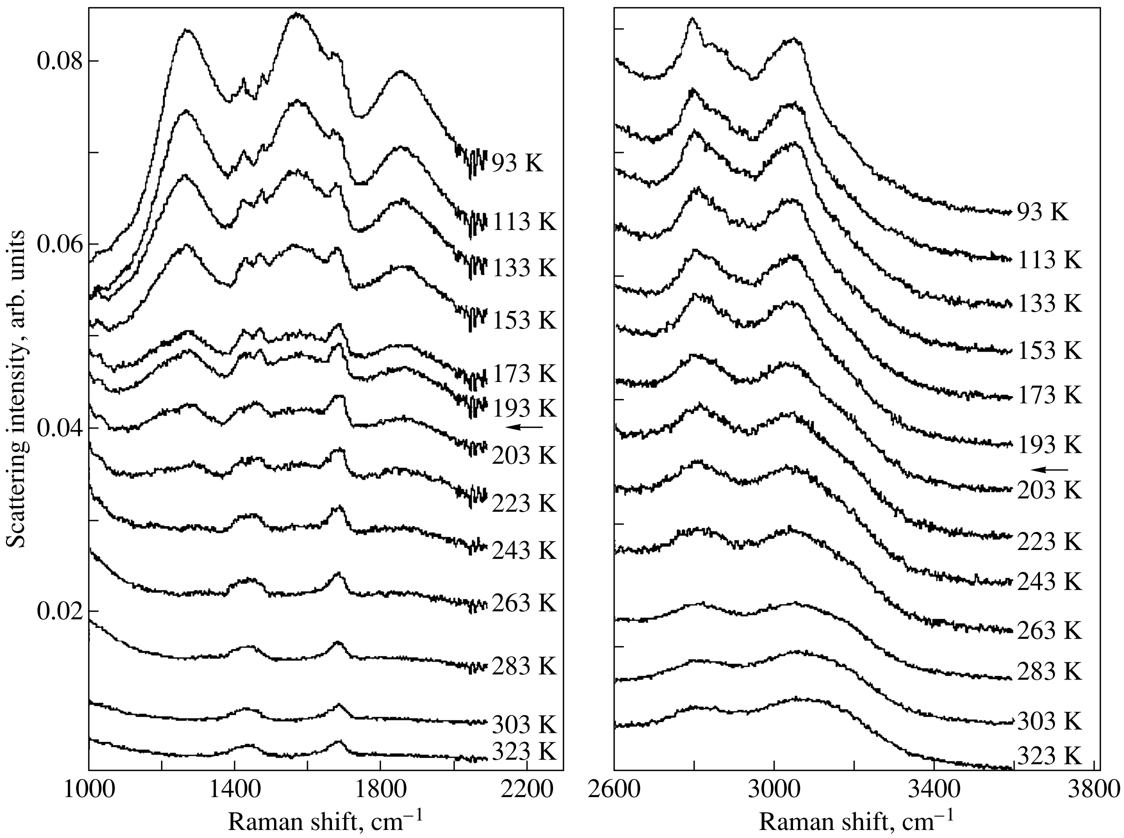

**Fig. 2.** Evolution of the spectra of internal vibrations of the ammonium ions during cooling.

The Raman spectrum in the range 750–1000 cm$^{-1}$ contains lines corresponding to the stretching vibrations of the W–O bonds in the $WO_3F_3^{3-}$ ions. The lines observed at frequencies below 500 cm$^{-1}$ are assigned to the stretching vibrations of the W–F bonds and to the bending vibrations of the $WO_3F_3^{3-}$ ions. The frequency of the most intense line (917 cm$^{-1}$) in the experimental Raman spectrum at room temperature nearly coincides with the calculated frequency (915 cm$^{-1}$ [6]) of the totally symmetric stretching vibrations of the W–O bond for the *cis* configuration of the $WO_3F_3^{3-}$ ion. The frequency of the complex line observed in the range 775–850 cm$^{-1}$ is close to the frequency of the doubly degenerate asymmetric stretching vibrations of the $WO_3F_3^{3-}$ ion in the same configuration (the calculated frequency is equal to 821 cm$^{-1}$). The calculated frequency (810 cm$^{-1}$) of the strong stretching vibrations of the W–O bond for the *trans* configuration of the $WO_3F_3^{3-}$ ion also falls in the aforementioned range. Judging from the shape of this line, it is a superposition of at least three single lines and involves two lines formed as a result of the lifting of the degeneracy of the $E$ vibrations of the $WO_3F_3^{3-}$ ion in the *cis* configuration and an intense line attributed to the $A_1$ vibrations of this ion in the *trans* configuration [6].

Below the phase transition temperature, the line at a frequency of 917 cm$^{-1}$ is drastically narrowed and is split into two lines (Fig. 3). The widths of these lines at temperatures far from the phase transition point remain almost unchanged. This suggests that the damping of the corresponding vibrations is determined by the ordering due to the phase transition rather than by their anharmonicity. Since these vibrations are nondegenerate, the appearance of the second lines indicates an increase (most likely, doubling) in the volume of the primitive cell of the structure.

Similar changes are observed for the line located in the range 775–850 cm$^{-1}$. Already at a temperature 1–2 K below the phase transition point, its three constituent lines are substantially narrowed and well resolved. As the temperature further decreases, each of these lines transforms into a doublet whose splitting increases and whose components narrow insignificantly. Similar changes, though not as pronounced, occur in the low-frequency spectral range.

It is obvious that the observed changes in the Raman spectrum are associated with the orientational ordering of the molecular anions. However, the ammonium cations remain orientationally disordered. This is respon-

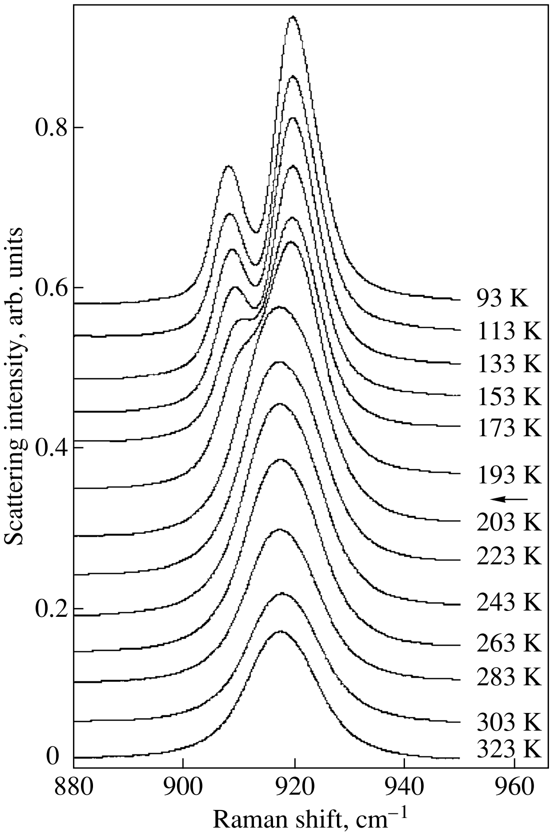

**Fig. 3.** Evolution of the line at 917 cm$^{-1}$ during cooling.

sible for the large widths of the lines corresponding to their internal vibrations. An enhanced interaction of the cations with the ordered anion sublattice leads to their noticeable distortion. It is quite probable that hydrogen bonds are formed between the ammonium protons and oxygen atoms of the ordered anion sublattice.

The experiments under high hydrostatic pressures (up to 9 GPa) at room temperature were performed on a setup equipped with diamond anvils. The diameter of the chamber containing the sample was equal to 0.25 mm, and the height of the chamber was 0.1 mm. The Raman spectra were excited by radiation from an Ar$^+$ laser (514.5 nm, 500 mW) and recorded on a Dilor OMARS 89 multichannel Raman spectrometer. Because of the strong diffuse scattering of light by the windows of the cell and the intense spectrum of the pressure-transmitting alcohol mixture, it was possible to measure reliably only the intense line at 917 cm$^{-1}$ (Fig. 1).

At pressures above ~1.3 GPa, the intensity of this line decreases sharply, whereas the frequency increases rapidly. These changes can indicate a phase transition. However, the line is not split. This suggests that the low-temperature phase differs from the high-pressure phase and that the corresponding phase transitions occur through different mechanisms. As the pressure further increases (up to 8.46 GPa), no indication of transient phenomena is revealed in the spectra.

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