

PHASE
TRANSITIONS

Raman Spectroscopic Study of the Lattice Dynamics in the $\text{Rb}_2\text{KMoO}_3\text{F}_3$ Oxyfluoride

A. S. Krylov^a, E. M. Merkusheva^a, A. N. Vtyurin^a, and L. I. Isaenko^b

^a Kirensky Institute of Physics, Siberian Branch of the Russian Academy of Sciences,
Akademgorodok 50–38, Krasnoyarsk, 660036 Russia

e-mail: shusy@iph.krasn.ru

^b Sobolev Institute of Geology and Mineralogy, Siberian Branch of Russian Academy of Sciences,
pr. Akademika Koptyuga 3, Novosibirsk, 630090 Russia

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Abstract—The lattice dynamics of the $\text{Rb}_2\text{KMoO}_3\text{F}_3$ oxyfluoride has been studied by Raman spectroscopy in the temperature range 7–400 K. A phase transition has been revealed at $T \approx 185$ K with decreasing temperature. Anomalies of the frequencies and Raman line half-widths have been analyzed. No condensation of soft lattice modes has been found. The character of changes in the Raman spectra of the $\text{Rb}_2\text{KMoO}_3\text{F}_3$ oxyfluoride shows that the phase transition is related to variations in the $[\text{MoO}_3\text{F}_3]^{3-}$ molecular octahedron.

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1. INTRODUCTION

The $\text{Rb}_2\text{KMoO}_3\text{F}_3$ oxyfluoride is a representative of a large family of perovskite-like oxyfluorides with the general formula $A_2A'MO_3F_3$ ($A, A' = \text{Rb}, \text{Cs}, \text{K}; M = \text{W}, \text{Mo}$). In the high-temperature phase, the representatives of the family have a structure of the elpasolite ($A \neq A'$) or cryolite ($A = A'$) type. The unit cell structure in the cubic phase is identical to that presented in [1]. $A_2A'MO_3F_3$ oxyfluorides differ from pure oxides and fluorides by a lower (noncubic) symmetry of the six-coordinated anion (quasi-octahedron). According to the *fac*- and *mer*-configurations of arrangement of ligands, the symmetry can be trigonal (C_{3v}) or orthorhombic (C_{2v}), respectively [2]. Because of the difference in the magnitudes of the F and O charges, each of the configurations must necessarily have a dipole moment. Despite the existence of a dipole moment in an individual octahedron, the macroscopic symmetry of the oxyfluoride crystal lattice is cubic with space group $Fm\bar{3}m$ ($Z = 4$) because of statistical disordering of the F and O atoms [2]. The interest in oxyfluorides is motivated by searching for compounds in which a macroscopic dipole moment exists by itself or due to phase transitions or external actions. The compounds with similar properties are studied by many research groups throughout the world [3–7], and they are widely used in various practical applications.

In [1, 6], it was shown that the $[\text{MO}_3\text{F}_3]^{3-}$ octahedron has predominantly the *fac*-configuration.

Depending on the ratio of the ionic radii R_A and $R_{A'}$ and also on the type of M atoms, the $Fm\bar{3}m$ structure can be distorted as a result of two [7–15] or one phase transition [1, 7, 11–14, 16], or it can remain stable down to the liquid-helium temperature [7, 11–14]. For instance, despite very close values of the ionic radii of Mo ($R_{\text{Mo}} = 0.073$ nm) and W ($R_{\text{W}} = 0.074$ nm) atoms, the $\text{Rb}_2\text{KMoO}_3\text{F}_3$ elpasolite undergoes a phase transition on cooling [17], while the $\text{Rb}_2\text{KW}\text{O}_3\text{F}_3$ elpasolite remains cubic and does not undergo any phase transformations.

In [2, 11–14, 18], it was found that the $\text{Rb}_2\text{KMoO}_3\text{F}_3$ elpasolite undergoes two successive phase transitions at $T = 328$ K (with appearance of a spontaneous polarization) and at $T = 182$ K. The studies of the compound were restarted several years ago. In [17], the properties of the $\text{Rb}_2\text{KMoO}_3\text{F}_3$ elpasolite were studied on many samples synthesized by various methods. It was shown that the oxyfluoride undergoes only one order–disorder ferroelectric phase transition from the cubic phase ($Fm\bar{3}m$, $Z = 4$) at $T = 195$ K far from the tricritical point. The structure of the low-temperature phase of the crystal is unknown up to now because of the twinning in the existing samples [17]. Thus, the problem was set up to determine the role of $[\text{MO}_3\text{F}_3]^{3-}$ molecular groups in the phase transition and to study in detail the low-temperature phase in the $\text{Rb}_2\text{KMoO}_3\text{F}_3$ elpasolite based on evolution of the Raman spectra.

Experimental values of the vibration frequencies of atoms in the high-temperature cubic phase G_1 and low-temperature phase G_2

Atomic vibrations		G_1	G_2
		ω, cm^{-1}	
I	Lattice vibrations		40
			56
		46	79
		77	91
			107
II	O–Mo–F	203	210
			217
III	O–Mo–O	296	300
		283	284
IV	Mo–F	379	366
		360	356
V	Mo–O		818
			823
		826	831
		844	849
		864	863
			873
		904	896
	908		

Note: G_1 is the high-temperature $Fm\bar{3}m$ phase ($T = 300$ K); G_2 is the low-temperature phase ($T = 100$ K).

2. SAMPLE PREPARATION AND EXPERIMENTAL TECHNIQUE

The total Raman spectra of the non-oriented $\text{Rb}_2\text{KMoO}_3\text{F}_3$ single crystal were measured on a Horiba Jobin Yvon T64000 Raman spectrometer. We used $1.5 \times 1.5 \times 1.5$ -mm-sized sample no. 7 with no visible inclusions, which was synthesized from the melt and described in [17]. The temperature studies were performed using an ARS CS204-X1.SS helium cryostat of closed cycle. The temperature was measured by indications of a calibrated LakeShore DT-6SD1.4L silicon diode. The accuracy of temperature stabilization was < 0.2 K, and that during hysteresis was < 0.05 K. The sample placed into an indium gasket was fixed on a coolant guide; thereafter, the cryostat was evacuated to 1.0×10^{-6} mbar. A single-mode Ar+ laser with wavelength $\lambda = 514.5$ nm was used as an excitation light source. The radiation power on the sample was 7 mW.

The spectra in the temperature range 7–400 K were measured at a step of 0.5 K. In the vicinities of the phase transition and during measurement of the ther-

mal hysteresis of the transition, the temperature step was 0.1 K.

To obtain the quantitative data on the positions and widths of the spectral lines with positions of the maximum at $\omega > 150 \text{ cm}^{-1}$, we used the shape of the Lorentzian profile similarly to [19]

$$I_L(A, \omega, \Gamma) = \frac{2}{\pi} \frac{I\Gamma}{4(x - \omega)^2 + \Gamma^2}, \quad (1)$$

where A is the intensity; ω is the frequency (cm^{-1}); Γ is the full width at half-height, x is the current coordinate (frequency, cm^{-1}). However, the spectra at $\omega < 150 \text{ cm}^{-1}$ are more correctly described using the profile described by the damping harmonic oscillator (DHO) function [20]:

$$I_{\text{DHO}}(A, \omega, \Gamma) = n(x, T) \frac{2I\omega^2\Gamma x}{(\omega^2 - x^2)^2 + 4\Gamma^2 x^2}, \quad (2)$$

where

$$n(\omega, T) = \begin{cases} \left[\exp\left(\frac{\hbar\omega c}{k_{\text{B}}T}\right) - 1 \right]^{-1} + 1, & \omega > 0, \\ \left[\exp\left(\frac{\hbar\omega c}{k_{\text{B}}T}\right) - 1 \right]^{-1}, & \omega < 0, \end{cases}$$

where c is the velocity of light. It should be noted that the parameters of the spectral lines with high ω obtained as a result of expansion by two above described methods coincide within the limits of experimental error.

3. RESULTS AND DISCUSSION

The total vibration spectrum of the crystal can arbitrarily be divided into several ranges corresponding to vibrations of various structural elements [18]:

- I—the lattice vibration range ($< 150 \text{ cm}^{-1}$);
- II—the range of deformation O–Mo–F vibrations (150 – 250 cm^{-1});
- III—the range of deformation O–Mo–O vibrations (250 – 235 cm^{-1});
- IV—the range of valence Mo–F vibrations (335 – 450 cm^{-1});
- V—the range of deformation Mo–O vibrations (800 – 940 cm^{-1}).

The transformation (Figs. 1 and 2) and total dynamics (Fig. 3) of the spectra of the $\text{Rb}_2\text{KMoO}_3\text{F}_3$ elpasolite in the temperature range 7–400 K demonstrate the existence of anomalies below $T \approx 185$ K (with decreasing temperature) corresponding to the phase transition related to ordering of the F/O atoms in the anion octahedron [17]. The Raman spectrum of the $\text{Rb}_2\text{KMoO}_3\text{F}_3$ oxyfluoride is substantially changed: because of the reduction of symmetry, new

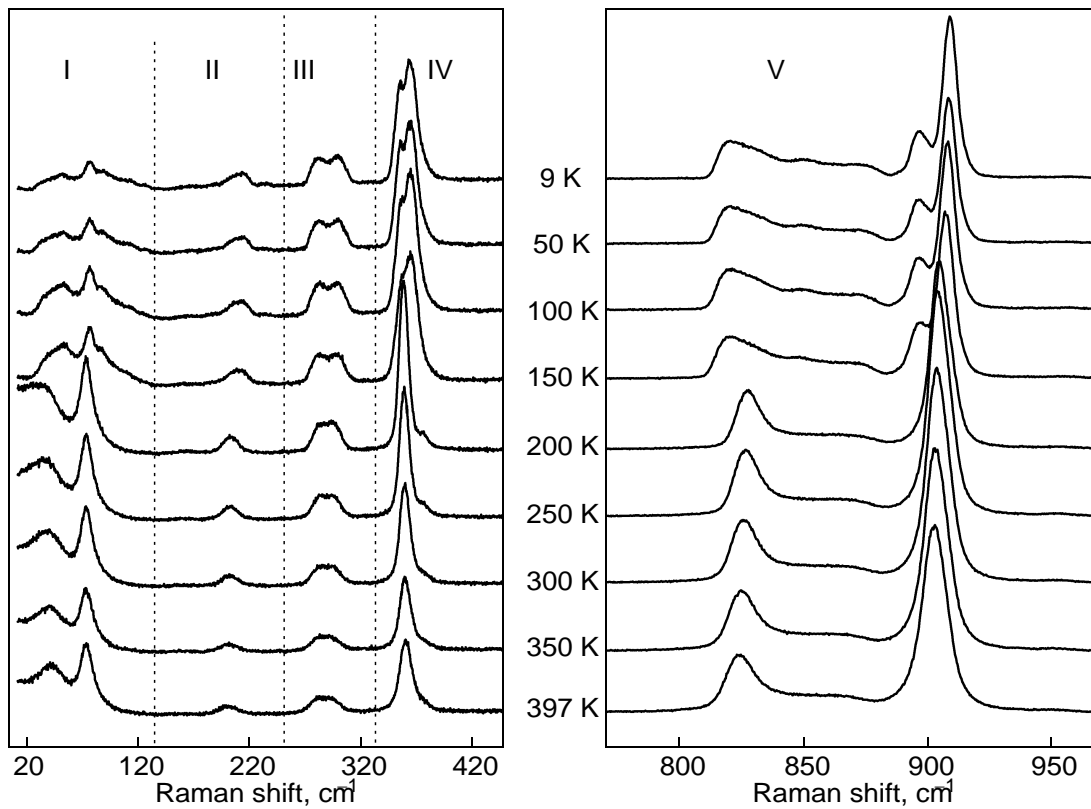


Fig. 1. Temperature transformation of the Raman spectra.

spectral lines appear; the line positions are significantly shifted, and there are anomalies in the behavior of the linewidths. Table lists the experimental frequencies of atomic vibration in the high-temperature cubic phase and in low-temperature phases.

The largest changes as a result of the phase transition occur in the frequency range corresponding to the valence vibrations of the Mo–O and Mo–F bonds, and also in the range of lattice vibrations (Fig. 1). The expansion of the spectrum into individual lines for temperatures lower and higher the phase transition temperature is shown in Fig. 2. It is clearly seen that, after the phase transition, the number of lines in the range of Mo–O vibrations is doubled. The splitting of line with a frequency of 904 cm^{-1} (at $T = 300 \text{ K}$) of the totally symmetric Mo–O vibration that is nondegenerate in the cubic phase indicates on the increase in the unit cell volume is at least doubled.

Along with the change in the spectral composition in the phase transition point, lines at frequencies of 904 and 361 cm^{-1} corresponding to the totally symmetric vibrations of the Mo–O and Mo–F bonds are shifted by 1.7 and 2.1 cm^{-1} , respectively; however, the shifts are opposite in sign.

In relation to significant change in the character of the temperature dependence of the frequency in the phase transition point, we extrapolated the tempera-

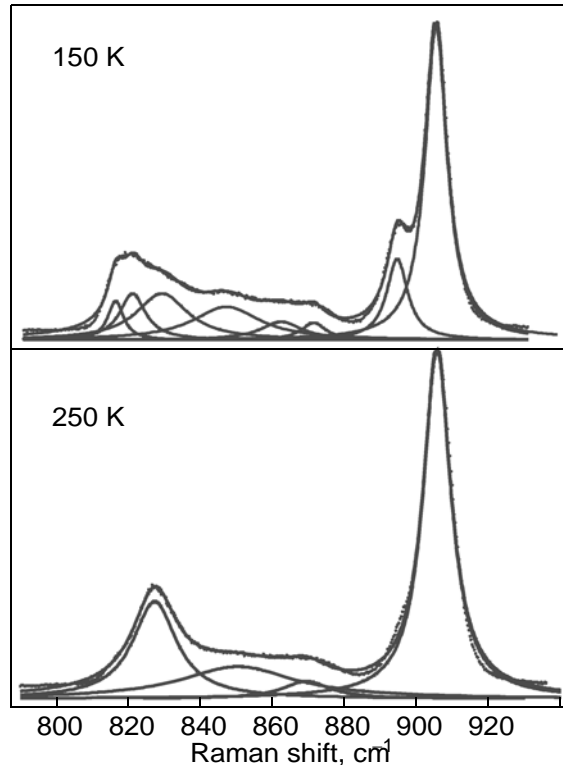


Fig. 2. Structure of the Raman spectra of the $\text{Rb}_2\text{KMoO}_3\text{F}_3$ elpasolite before and after the phase transition.

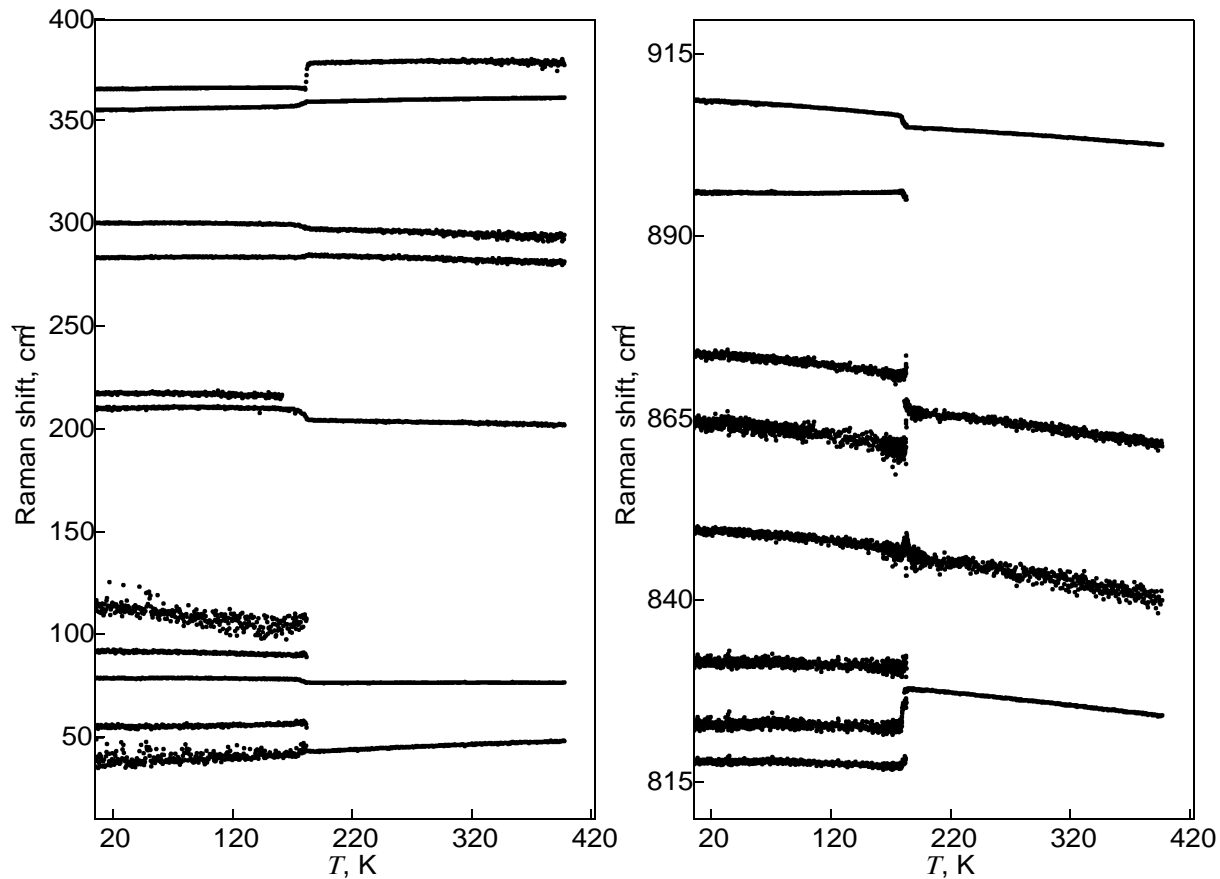


Fig. 3. Temperature dependences of the vibration frequencies of atoms of the $\text{Rb}_2\text{KMoO}_3\text{F}_3$ elpasolite.

ture run of the frequency and linewidth in the cubic phase by known dependences [21] that appear due to anharmonicity of the vibrations:

$$\omega(T) = \omega_0 + A \left(1 + \frac{2}{e^x - 1} \right) + B \left(1 + \frac{3}{e^y - 1} + \frac{3}{(e^y - 1)^2} \right), \quad (3)$$

$$\Gamma(T) = \Gamma_0 + C \left(1 + \frac{2}{e^x - 1} \right) + D \left(1 + \frac{3}{e^y - 1} + \frac{3}{(e^y - 1)^2} \right), \quad (4)$$

where

$$x = \frac{\hbar \omega_0 c}{2k_B T}, \quad y = \frac{\hbar \omega_0 c}{3k_B T}.$$

The constants have the values as follows: for the Mo–O bond, $\omega_0 = 906.4 \text{ cm}^{-1}$, $\Gamma_0 = 0.04 \text{ cm}^{-1}$, $A = -0.25 \text{ cm}^{-1}$, $B = 0.018 \text{ cm}^{-1}$, $C = 6.49 \text{ cm}^{-1}$, $D = 59.47 \text{ cm}^{-1}$; for the Mo–F bond, $\omega_0 = 355.2 \text{ cm}^{-1}$,

$\Gamma_0 = 0.009 \text{ cm}^{-1}$, $A = 0.44 \text{ cm}^{-1}$, $B = -0.005 \text{ cm}^{-1}$, $C = 8.73 \text{ cm}^{-1}$, $D = -4.06 \text{ cm}^{-1}$.

In Eqs. (3) and (4), the second term describes the decay of the optical phonon into two identical phonons (three-phonon interaction); the third term describes the decay of the optical phonon into three identical phonons, and ω_0 is the internal frequency of the optical phonon in the Brillouin zone center in a harmonic approximation.

The shift of the frequency of the longitudinal Mo–O mode with respect to the extrapolated value below the point of transition to the low-temperature phase is shown in Fig. 4a. At temperatures exceeding the phase transition temperature, the experimental dependence agree well with the theoretical that (Eq. (3)); then, an abrupt jump of the frequency occurs. According to [22], for the totally symmetric high-frequency vibrations, the frequency shift $\Delta\omega$ is proportional to the squared order parameter. The corresponding dependence shown in the inset to Fig. 4a demonstrates the behavior characteristic of first-order phase transitions far from the tricritical point. This result agrees well with the data from [17]. Similar procedure was performed for the Mo–F vibration (Fig. 4b).

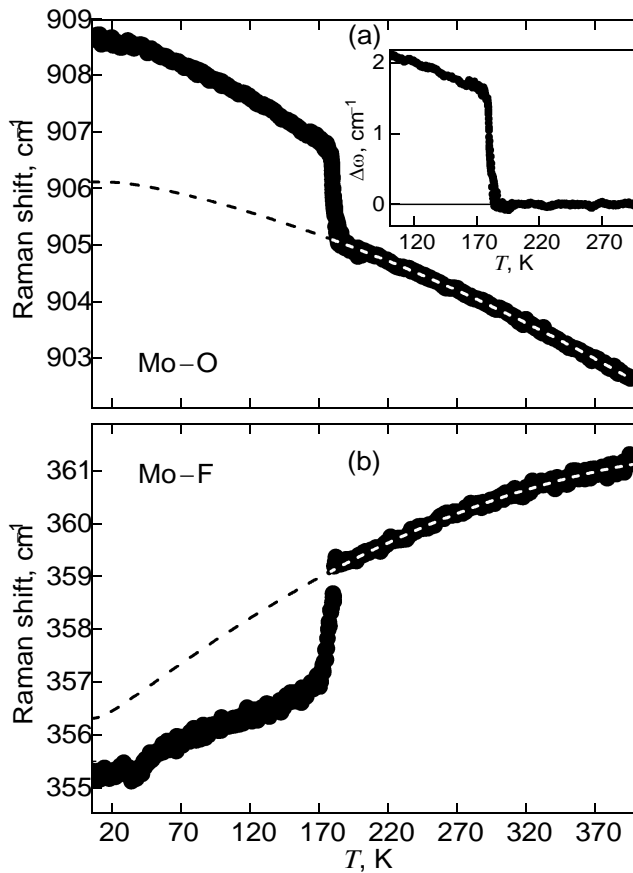


Fig. 4. Temperature dependences of the frequencies of the totally symmetric (a) Mo–O and (b) Mo–F vibrations.

The widths of these lines also are markedly changed with temperature. Their temperature dependences are depicted in Fig. 5. We see a pronounced anomalous λ -shape behavior of the linewidths of the totally symmetric Mo–O vibration (Fig. 5a) and, to a lesser degree, the totally symmetric Mo–F vibration (Fig. 5b). Similar anomalous dependence is characteristic of order–disorder phase transitions [23], and it appears due to an increase in order parameter fluctuations in the vicinity of the phase transition. According to [24], the λ -shape temperature dependence of the linewidth correlates with the behavior of the thermodynamic characteristics, i.e., the heat capacity, during the phase transition, since the vibration frequency as a microscopic characteristic of the crystal reflects the critical fluctuations of the order parameter. The curve shown in Fig. 5 is a result of extrapolation of the linewidth values in the cubic phase by Eq. (4). It is seen that the experimental dependence of the half-width near the phase transition and below is not described only by influence of anharmonic phonon–phonon interactions, which demonstrates that there are substantial contributions of other mechanisms of broadening the lines, in particular, a structural disordering

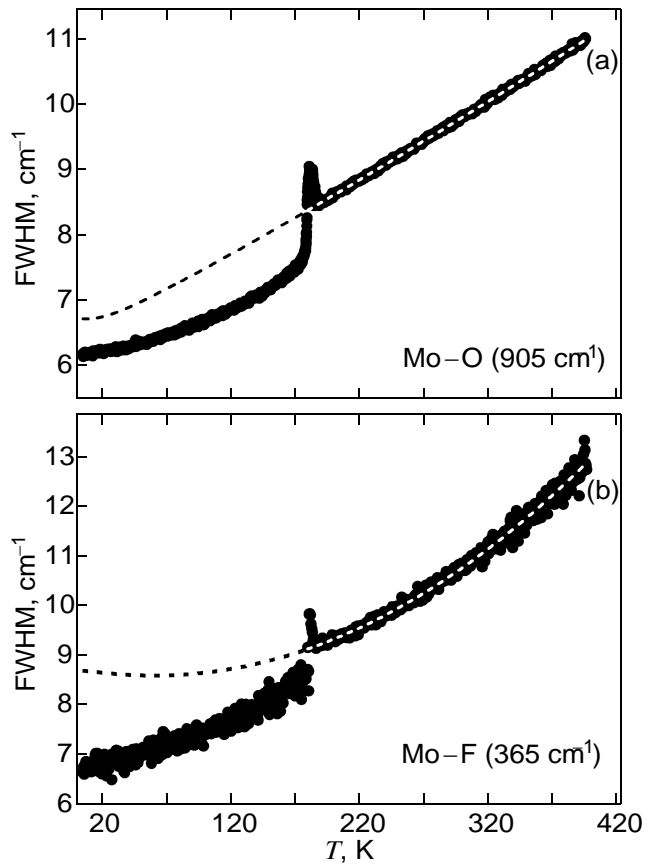


Fig. 5. Temperature dependences of the linewidths of the totally symmetric (a) Mo–O and (b) Mo–F vibrations.

of the crystal, and their anomalous changes in the transition point.

To study such a behavior in more detail, the region corresponding to the Mo–O vibrations (904 cm^{-1}) in the vicinity of the phase transition temperature was studied with a higher spectral resolution and smaller

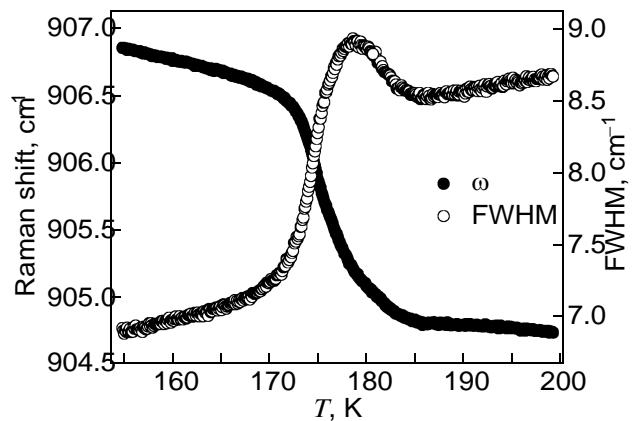


Fig. 6. Temperature dependences of the frequency and the linewidth of the totally symmetric Mo–O vibration.

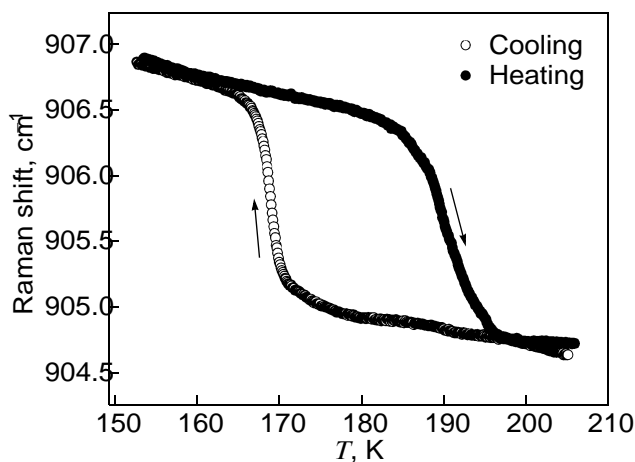


Fig. 7. Frequency of the totally symmetric Mo–O vibration measured during heating and cooling in the vicinity of the phase transition.

temperature step. The obtained temperature dependences of the frequency and the linewidth of the totally symmetric Mo–O vibration are shown in Fig. 6.

There is a phase transition hysteresis (Fig. 7). Since the phase transition region is smeared and is ~ 5 K, the correct determination of the hysteresis magnitude has a problem. As is seen from Fig. 7, $\Delta T = 20$ K.

4. CONCLUSIONS

The Raman spectra have been measured and interpreted. The experiment shows that the compound undergoes the structural phase transition at the temperature $T \approx 185$ K. Based on the behavior of the frequency shift proportional to the order parameter and changes in the shapes of the spectral lines, this phase transition is a first-order order–disorder transition that is connected with ordering of the F/O anions.

The character of changes in the Raman spectra of the $\text{Rb}_2\text{KMoO}_3\text{F}_3$ oxyfluoride shows that the phase transition at $T \approx 185$ K is related to changes in the $[\text{MoO}_3\text{F}_3]^{3-}$ molecular octahedron, and the splitting of the lines of nondegenerate vibrations allows the statement that the crystal unit cell volume increases during the phase transition.

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