

Infrared Absorption Investigation of the Role of Octahedral Groups upon the Phase Transition in the $\text{Rb}_2\text{KMoO}_3\text{F}_3$ Crystal

Yu. V. Gerasimova^{a,*}, A. S. Oreshonkov^a, A. N. Vtyurin^a, A. A. Ivanenko^a,
L. I. Isaenko^b, A. A. Ershov^a, and E. I. Pogoreltsev^a

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

* e-mail: jul@iph.krasn.ru

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

Received April 15, 2013

Abstract—The infrared absorption spectra of the oxyfluoride $\text{Rb}_2\text{KMoO}_3\text{F}_3$ have been measured in the frequency range corresponding to stretching vibrations of the Mo–O anion octahedron with the purpose of clarifying their role in the phase transition. A semi-empirical calculation of two possible configurations of quasi-octahedral MoO_3F_3 groups has been performed. The results of the investigations have demonstrated that some octahedra in the crystal structure change the local symmetry from C_{3v} to C_{2v} due to the phase transition ($T = 197$ K).

DOI: 10.1134/S1063783413110097

1. INTRODUCTION

The study of compounds with polar molecular groups in their structure becomes increasingly urgent in connection with the search for polar media featuring pyroelectricity, ferroelectricity, and piezoelectricity, as well as with the search for new active materials for electro- and nonlinear optics. One representative of such compounds is the oxyfluoride $\text{Rb}_2\text{KMoO}_3\text{F}_3$ crystal. According to an X-ray diffraction analysis, the $\text{Rb}_2\text{KMoO}_3\text{F}_3$ lattice at room temperature has cubic symmetry with space group $Fm\bar{3}m$ ($Z = 4$) (Fig. 1a [1]).

At the same time, fac- and mer-configurations [2] (Fig. 1b) of the arrangements of oxygen and fluorine ligands correspond to trigonal C_{3v} or orthorhombic C_{2v} symmetry of pseudo-octahedral MoO_3F_3 groups. Since both configurations are noncentrosymmetric, these molecular groups should have significant dipole moments in the nonpolar phase $Fm\bar{3}m$. To retain the macroscopic cubic symmetry of the crystal, anionic groups should be disordered in orientation. However, their complete or partial ordering can be expected in the case of crystal structure distortion, e.g., due to the phase transition.

In [2–7], two successive phase transitions, at 328 and 182 K, were detected in $\text{Rb}_2\text{KMoO}_3\text{F}_3$ crystals; and both distorted phases were polar. In later studies [1], only one phase transition to the nonpolar low-temperature phase was observed in this compound at 195 K. The experimental Raman spectroscopic study

of this crystal [8] confirmed the existence of the structural phase transition at ~ 185 K. Based on an analysis of the temperature dependence of the frequency shift proportional to the order parameter and changes in the spectral line shape, it was found that quasi-octahedra $[\text{MeO}_3\text{F}_3]^{3-}$ are mostly in the fac-configuration, and this phase transition is the first-order order–disorder-type phase transformation accompanied by F/O anion ordering.

The present study of infrared spectra of the $\text{Rb}_2\text{KMoO}_3\text{F}_3$ crystal was undertaken to further investigate the role of octahedral anions during the structural phase transition.

2. EXPERIMENTAL TECHNIQUE AND DATA PROCESSING

The experiments on IR absorption were performed on oxyfluoride $\text{Rb}_2\text{KMoO}_3\text{F}_3$ samples described in [1].

The IR absorption spectra were measured on pellets ≈ 0.55 mm thick and 13 mm in diameter, pressed together with potassium bromide, using a Bruker-Vertex 80V vacuum Fourier spectrometer. $\text{Rb}_2\text{KMoO}_3\text{F}_3$ microcrystals were carefully powdered and mixed with KBr also carefully ground in a proportion of 1 : 100, respectively.

The mixture was pressed under vacuum by a hydraulic press at pressures from 10 to 10^4 N/cm². The spectral resolution was 0.2 cm⁻¹. The thermal study was performed using an OptistatTM AC-V 12a

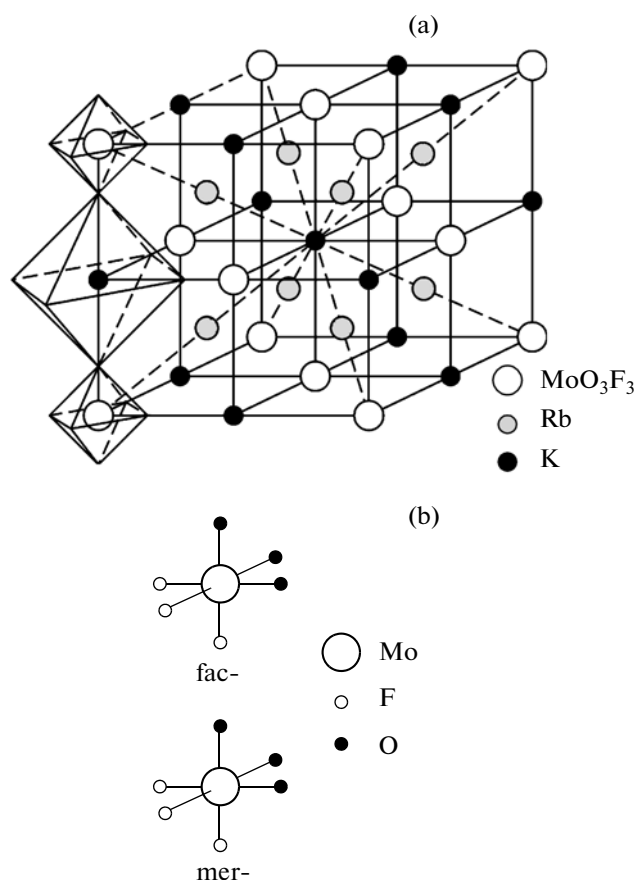


Fig. 1. (a) Structure of the unit cell of the cubic phase of the $\text{Rb}_2\text{KMoO}_3\text{F}_3$ crystal and (b) local symmetry of the $\text{MoO}_3\text{F}_3^{3+}$ octahedral ion.

0.25W@4K cryostat in the temperature range of 298–188 K. The light source was a globar (*U*-shaped arc made of silicon carbide) emitting mid-IR radiation.

3. EXPERIMENTAL RESULTS AND DISCUSSION

Figure 2 shows the room-temperature measured IR spectrum of the $\text{Rb}_2\text{KMoO}_3\text{F}_3$ crystal in the frequency range of 500–1500 cm^{-1} . The spectral lines in the frequency range of 775–925 cm^{-1} correspond to Mo–O stretching vibrations of the MoO_3F_3 anion polyhedron. It should be noted that the frequencies of IR spectrum and Raman spectrum [8] lines coincide; this suggests that the nonpolar cubic phase already contains polar regions in which the center of symmetry is absent.

The spectrum transformation with decreasing temperature is shown in Fig. 3; it reveals the presence of anomalous changes below 197 K and confirms the existence of the phase transition associated with changes in the fluorine–oxygen quasi-octahedron.

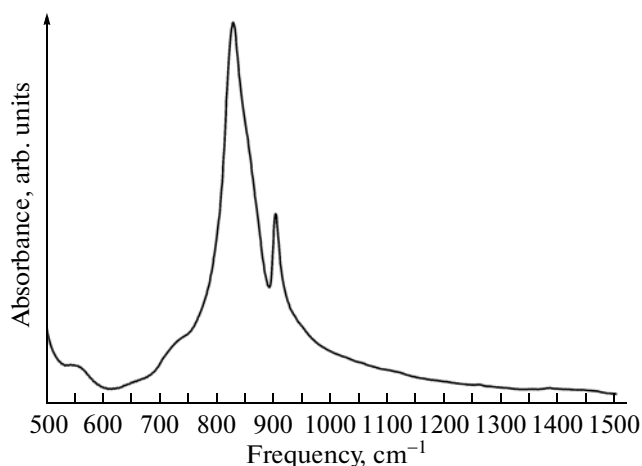


Fig. 2. Room-temperature IR spectrum of the $\text{Rb}_2\text{KMoO}_3\text{F}_3$ crystal.

Since the MoO_3F_3 anion can have both C_{3v} and C_{2v} symmetry, a semi-empirical calculation of the vibration spectrum of the localized MoO_3F_3 octahedron was performed using the LADY software package [9]. To calculate ion–ion interactions, the simplified Born–Karman model [10] was used. This model is based on the potential function representation as a sum of interaction potentials $\varphi(r)$ of structural units, which depend only on the distances between them. In this case, only bond stretching (compression) force constants $A = \partial^2 E / \partial^2 R$, where E is the energy and R is the bond length are taken into account. Within the simplified Born–Karman model, it is assumed that the form of the pair short-range interaction potential $\varphi(r)$ is identical for all atom pairs

$$A = \lambda \exp(-r_{ij}/\rho), \quad (1)$$

where r_{ij} is the interatomic distance and λ is the empirical parameter characterizing the interaction of a given atom pair. To determine the parameters of the calculation model, a program for optimizing λ and ρ was developed.

The result of numerical simulation showed that two lines at 836 and 907 cm^{-1} should be observed in the IR absorption spectrum if the anion polyhedron has a fac-configuration; in the case of a mer-configuration, lines with maxima at 798, 881, and 891 cm^{-1} should take place. A comparison of the experimental data with calculated spectra of two possible configurations (Fig. 4) shows that none of them separately describe completely the spectral profile. However, it can be noted that the result of numerical simulation of the fac-configuration is closest to the experimental spectra measured above the phase transition point (Fig. 4a). Certain asymmetry of the line at 828 cm^{-1} can be associated with partial removal of degeneracy of this doubly degenerate vibration due to structural disorder of the cubic phase.

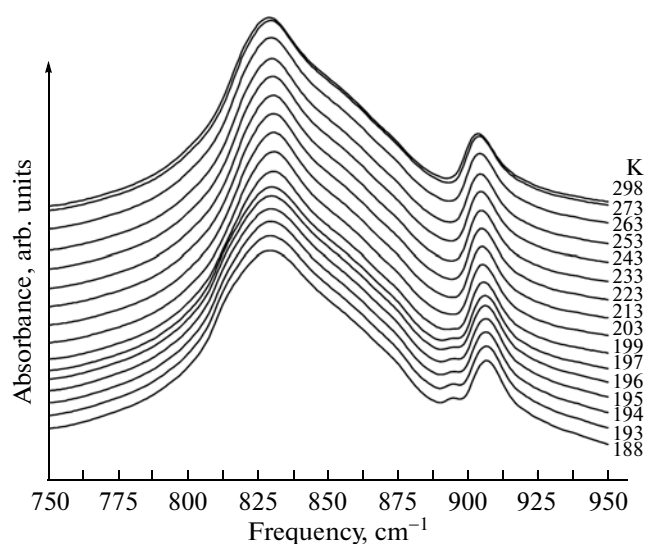


Fig. 3. Transformation of IR absorption lines corresponding to Mo–O stretching vibrations of $\text{MoO}_3\text{F}_3^{3-}$ anions during the phase transition.

As the temperature decreases below the transition point, the situation changes: additional lines appear in the spectral profile, which are characteristic of the mer-configuration of the ion (Fig. 4c). In the spectral region corresponding to Mo–O stretching vibrations, lines of both fac- and mer-configurations present in the distorted crystal phase; in this case, before the phase transition, quasi-octahedra in the structure had preferentially C_{3v} symmetry; below the transition, some of these quasi-octahedra, probably, gained C_{2v} symmetry.

The dipole moment of the fac-configuration is directed along one of the threefold axes of the cubic cell, and in the case of the mer-configuration, along one of the fourfold axes. Thus, in addition to the dipole moment itself (which exists in the cubic phase in either configuration), polar phase formation requires the formation of long-range correlation of orientations of these dipole moments. It can be assumed that mer-polyhedra formed although in small amounts prevent the ordering process.

4. CONCLUSIONS

The infrared absorption spectra of oxyfluoride $\text{Rb}_2\text{KMoO}_3\text{F}_3$ in the region of stretching vibrations of Mo–O bonds of the MoO_3F_3 anion octahedron were measured and interpreted. The frequency positions of the IR spectrum and Raman spectrum lines coincide, which suggests that the nonpolar cubic phase already contains local polar regions.

The semi-empirical calculation of two possible configurations of this octahedron was performed. A comparison of changes in IR spectra, experimentally

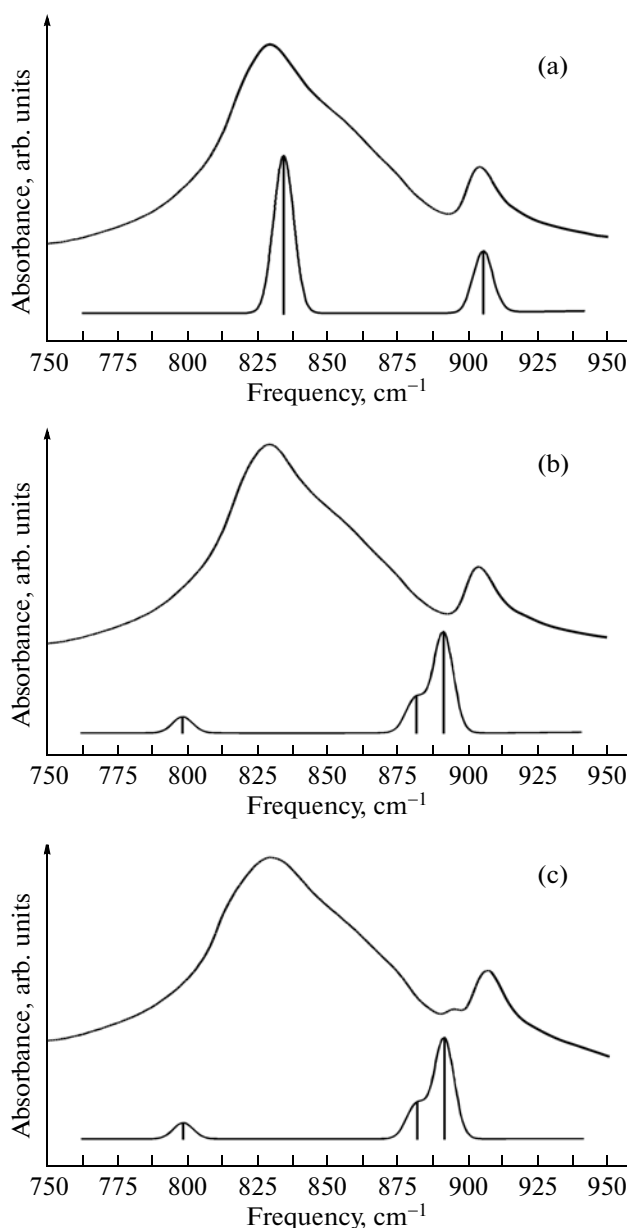


Fig. 4. Comparison of the experimental spectra with the calculated spectra of possible octahedron configurations at various temperatures: (a) $T = 298$ K, fac-configuration; (b) $T = 298$ K, mer-configuration; and (c) $T = 188$ K, mer-configuration.

observed during the phase transition, with the results of numerical simulation shows that the phase transition at 197 K is associated with a partial change in the configuration and symmetry of fluorine–oxygen pseudo-octahedra.

ACKNOWLEDGMENTS

This study was supported by the Russian Foundation for Basic Research (project no. 12-02-31205_mol_a), the Ministry of Education and Sci-

ence of the Russian Federation within the framework of the Russian Federal Target Program “Scientific and Scientific–Pedagogical Human Resources for the Innovative Russia” (agreement no. 8379), and the Interdisciplinary Integration Project of the Siberian Branch of the Russian Academy of Science No. 28.

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Translated by A. Kazantsev