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Nonempirical Calculations of $K_3WO_3F_3$ Cryolite Lattice Dynamics

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Vibrational frequencies of $K_3WO_3F_3$ cryolite have been calculated for Fm3m, I4 mm, Cm structures in the framework of generalized Gordon–Kim model with account of quadrupole polarizabilities. The phonon spectra have been found to have "soft" modes with eigenvectors in agreement with experimental atomic displacements.

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Introduction

$K_3WO_3F_3$ cryolite belongs to a rather large group of oxyfluorides with chemical formula $A_2A'WO_3F_3$ (A, A' = K, Rb, Cs).

Oxyfluorides $A_2A'WO_3F_3$ differ from "pure" oxides and fluorides by lower (noncubic) symmetry of WO_3F_3 pseudo-octahedron groups. The symmetry of WO_3F_3 groups, according to *cis* and *trans* configurations of ligands arrangement, can be trigonal (C_{3v}) and orthorhombic (C_{2v}), respectively. Meanwhile, oxyfluorides with general chemical formula $A_2A'WO_3F_3$ (A, A' = K, Rb, Cs) are specified at high temperature by cubic elpasolite–cryolite structure ($Fm3m$) caused by statistical disordering of the oxygen and fluoride atoms.

Compounds with equivalent cations $A = A'$ (cryolites) undergo a succession of two phase transitions of ferroelectric and ferroelastic nature. Usually, it can be explained by atomic displacements, which give rise to both spontaneous polarization and spontaneous deformation. $K_3WO_3F_3$ cryolite studied in this work, undergoes two successive phase transitions at $T_1 = 414$ K and $T_2 = 452$ K [1]. Recently [2] the symmetry group was shown to change under cooling as follows: $Fm3m \rightarrow I4mm \rightarrow Cm$. Experimental lattice parameters and atomic coordinates of atoms are also presented in [2]. Changes of lattice parameters for every structure are shown in Table 1.

In this work we apply generalized Gordon–Kim method [3] to simulate lattice dynamics of $K_3WO_3F_3$.

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Table 1
Changes of symmetry and lattice parameters at phase transitions [2].

Fm3m	$a = a_0$	$b = b_0$	$c = c_0$	$a = b = c = 8.796$ Å
I4mm	$a = (a_0 - b_0)/2$	$b = (a_0 + b_0)/2$	$c = c_0$	$a = b = 6.167$ Å $c = 8.799$ Å
Cm	$a = a_0$	$b = b_0$	$c = (c_0 - a_0)/2$	$a = 8.735$ Å $b = 8.690$ Å $c = 6.157$ Å

Calculations and Results

As WO_3F_3 groups may have two configurations, lattice dynamics were calculated for fully ordered structures, where the octahedra have *cis* or *trans* configurations. From the energy minimum lattice parameters and atomic coordinates have been found for these ordered structures: rhombohedral (a, c) for C_{3v} symmetry, and orthorhombic (a, b, c) for C_{2v} symmetry. Similar calculations were carried out with cubic lattice parameters. These results are presented in Table 2. Vibrational frequencies were also calculated for both ordered structures (Table 2). Our calculations of lattice dynamics show, that these fully ordered structures are unstable; their vibrational spectra were found to have "soft" modes. In the experimental Raman spectrum [4] the number of peaks in the high frequency range is bigger than is possible for an ordered cryolite structure. This fact may be due to existence of octahedron groups both in *cis* and in *trans* configuration simultaneously. As apparent from Table 3, calculated frequency values of the two highest modes of the orthorhombic structure are between the frequency values of the two highest modes of the rhombohedral structure, which is in agreement with the experiment [(Fig. 1)].

The calculated lattice parameters of the rhombohedral and orthorhombic structures are very close to the cubic lattice parameters; the differences are less than 0.5%. The rhombohedral structure is more energy-favorable both with minimal lattice parameters and the cubic lattice parameters (Table 3). So further on all octahedra were assumed to have only

Table 2
Phonon spectra of ordered structure of $K_3WO_3F_3$ cryolite

cis configuration ω (cm^{-1})		trans configuration ω (cm^{-1})		
86.*1i*(2)	161.2	87.9*i*	109.1	239.4
67.*8i*(2)	177.8	80.4*i*	120.2	239.8
25.4	207.7(2)	59.1*i*	123.5	303.7
43.3(2)	244.5(2)	34.5	164.4	431.9
45.3	272.4	35.2	165.0	461.8
95.3(2)	469.3(2)	41.8	168.9	481.8
111.9	496.4	49.2	198.9	501.3
136.8(2)	510.8(2)	81.1	201.6	520.6
141.0	573.8	97.2	233.2	541.7

Table 3
Cubic lattice parameters, lattice parameters of ordered structure, and crystal energy for each set of $K_3WO_3F_3$ cryolite parameters

	trans	cis
	cubic	
a_i, Å	*8,76*	*8,76 ($a = 6,19; c = 15,18$)*
E_{cub}, eV.	−257.1635	−257.2255
	Minimum	
a_i, Å	$a = 8.74; b = 8.76; c = 8.76$	$a = 6,17; c = 15,24$
E_{min}, eV	−257.1905	−257.2278

cis configurations but different orientations. Under this assumption, statistical disordering is modeled by the following scheme (Fig. 2).

To simulate an "average" spectrum of the *Fm*3*m* structure, dynamical matrix of the ordered crystal is calculated for all eight possible orientations of the octahedron groups (Fig. 2a). These results are averaged numerically, and then eigenvalues of "average" dynamical matrix—frequencies of atomic vibrations and their eigenvectors—are found. In the "average" *Fm*3*m* structure "soft" mode was found. As evident from Table 2, the eigenvectors of the "soft" mode agree with the experimental atomic displacements at the phase transition.

The "average spectra" were also calculated in a similar manner for the lower temperature structure *I*4*mm*. For this structure dynamical matrix of the ordered crystal is calculated only for four configurations of octahedra shown in Figure 2b. Here, the "soft" mode of the vibrations was also found. Analogous data for the eigenvectors of this "soft" mode are presented in Table 4 with experimental atomic displacements at the second phase transition.

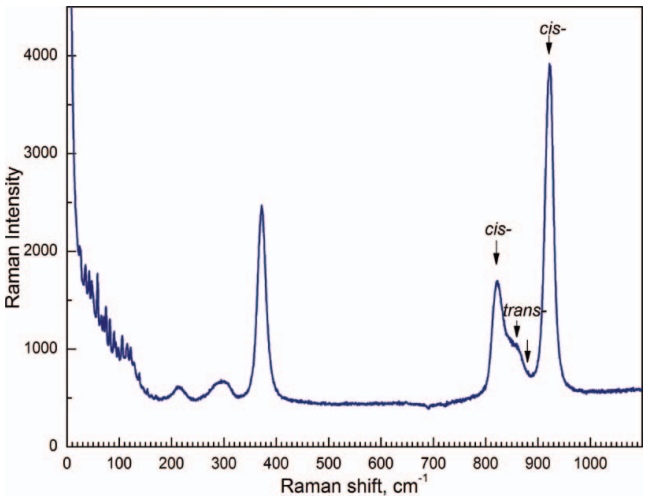

Figure 1. Raman spectrum of $K_3WO_3F_3$ cryolite.

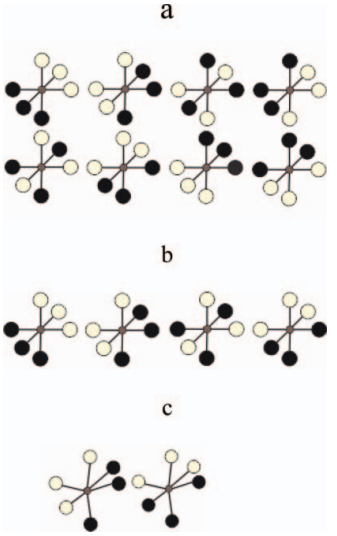

Figure 2. Octahedron groups orientation: a – *Fm*3*m*; b – *I*4*mm*; c – *Cm*

From this Table it is apparent, that the displacement type is very much the same as at phase transitions *Fm*3*m* → *I*4*mm*, but the vector has both *x* and *z* components.

Calculations of the "average" vibrational frequencies in the *Cm* structure also show presence of unstable modes. This is assumed to be due to experimental values [2] of

Table 4
Eigenvectors of "soft" modes and experimental atomic displacements

	Experimental atomic displacements	Eigenvectors of "soft" modes
*Fm*3*m*–>*I*4*mm*	$K_1(0a; 0b; 0.012c)$	$K_1(0a; 0b; 0.30c)$
	$K_2(0a; 0b; 0.012c)$	$K_2(0a; 0b; 0.30c)$
	$K_3(0a; 0b; 0.003c)$	$K_3(0a; 0b; 0.175c)$
	O/F$(0a; 0b; 0.026c)$	O/F$(0a; 0b; 0.065c)$
	O/F$(0a; 0b; 0.026c)$	O/F$(0a; 0b; 0.085c)$
	O/F$(0a; 0b; 0.026c)$	O/F$(0a; 0b; 0.067c)$
	O/F$(0a; 0b; 0.026c)$	O/F$(0a; 0b; 0.051c)$
	O/F$(0a; 0b; 0.026c)$	O/F$(0a; 0b; 0.031c)$
	O/F$(0a; 0b; 0.026c)$	O/F$(0a; 0b; 0.074c)$
*I*4*mm*–>*Cm*	$K_1(0.021a; -0.031b; -0.027c)$	$K_1(0.038a; 0b; 0.038c)$
	$K_2(0.021a; 0.031b; -0.027c)$	$K_2(-0.638a; 0b; -0.638c)$
	$K_3(-0.025a; 0b; -0.032c)$	$K_3(-0.06a; 0b; -0.06c)$
	O/F$(0.03a; 0b; 0.009c)$	O/F$(-0.04a; 0b; 0.125c)$
	O/F$(-0.03a; 0b; 0.009c)$	O/F$(0.125a; 0b; -0.04c)$
	O$(0a; 0b; 0c)$	O$(0.287a; 0b; 0.287c)$
	O/F$(-0.03a; 0b; -0.026c)$	O/F$(-0.032a; 0b; 0.071c)$
	O/F$(-0.03a; 0b; 0.007c)$	O/F$(0.071a; 0b; -0.032c)$
	F$(0a; 0b; 0.02c)$	F$(-0.039a; 0b; -0.039c)$

atom coordinates used to calculate the energy and lattice dynamics of this structure, while in the cubic and tetragonal structures, where the free parameters are few, the calculated coordinates could be found from the equilibrium condition.

Conclusions

The work studied lattice dynamics of $K_3WO_3F_3$ cryolite by generalized Gordon—Kim method. The structures with *cis* octahedra configuration have been found to be more energy-favorable. The phonon spectra for the two ordered structures were calculated. Both spectra have "soft" modes and distribution of the values of the highest modes of the rhombohedral and orthorhombic structures are in good agreement with experiment. "Average" phonon spectra of *Fm*3*m*, *I*4*mm* and *Cm* structures have been calculated. All these structures are not stable; their spectra include unstable "soft" modes. Eigenvectors of these "soft" modes for *Fm*3*m* and *I*4*mm* structures agree with experimental atomic displacements.

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