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Symmetry analysis of calculated vibrational spectra of Rb_2KScF_6 crystal

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Abstract

To interpret the recent results of Raman scattering soft mode below phase transitions in Rb_2KScF_6 elpasolite-like crystal, results of ab initio simulations of its lattice dynamics obtained within modified Gordon–Kim approach, are used. Calculated eigenvectors of lattice normal modes are attributed to experimental lines using projector operator method. It is shown that the complicated behavior of the soft mode in the lower temperature phase of the crystal is due to its interaction with "hard" vibrations of Rb^+ ions.
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1. Introduction

Elpasolites A_2BCX_6 (high symmetry phase G_0, space group $Fm3m$, $Z = 4$, unit cell structure is shown in Fig. 1), are one of the perovskite-like family of crystals that are extensively studied for their wide variety of structures and excitedly complicated sequences of phase transitions [1]. Their structural phase transitions are usually connected with lattice instability due to rotations of CX_6 octahedra arising from condensation of soft phonons. For a very long time softening of such lattice modes was known only in bromine-, chlorine- and oxygen-containing elpasolites (see, e.g., [2–5]). First experimental investigation of phase transitions in fluorine-containing elpasolite did not reveal any soft modes

[6], and only recently some anomalies in the lower frequency part of the Raman spectrum of Rb_2KScF_6 crystal have been observed under cooling below transition points [7]. However, the obtained temperature dependencies appear far more complex than the classic soft mode behavior $\Omega^2 \sim \Delta T$. (Sequence of phase transitions for this crystal under cooling: $T_1 = 252$ K (into G_1 phase, space group $I114/m$, $Z = 2$) and $T_2 = 223$ K (into G_2 phase, space group $P12_1/n1$, $Z = 2$) [8]. Ab initio simulations of lattice stability for this crystal have shown [9,10] that soft mode condensation could induce these phase transformations, and perfect agreement between calculated and experimental transition temperature has been obtained.

The aim of this paper is to analyze the results of ab initio crystal lattice dynamics simulations [9,10] and apply them to the interpretation of experimental data of Raman scattering in Rb_2KScF_6 crystal near transition temperature.

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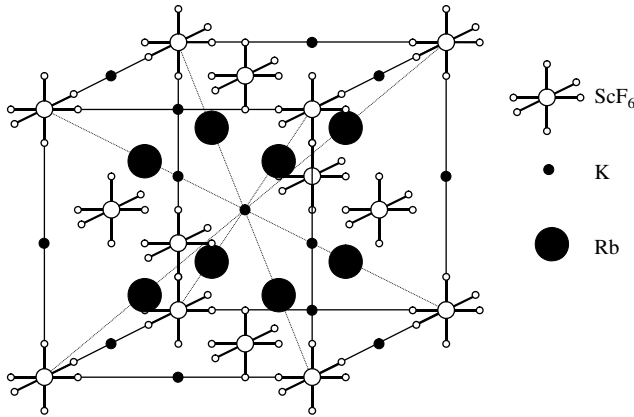 *E-mail address:* slanky@iph.krasn.ru (S.N. Krylova).

Fig. 1. Structure of the cubic phase (phase G_0, space group $Fm3m$, $Z = 4$) of Rb_2KScF_6 crystal.

Fig. 3. Temperature dependencies of squared frequencies for low lying lattice modes appear below phase transitions.

2. Experiment

Samples for experiments ($2 \times 2 \times 4\,mm^3$, optically transparent and without colored defects or inclusions) were taken from the same crystallization as in [7] and cut along crystallographic axes of the cubic phase. Back scattering Raman spectra were obtained with T-64000 Raman spectrometer (ISA, Jobin Yvon) with nitrogen-cooled CCD detector. To reduce low frequency wing of elastic scattering the low frequency spectra have been registered in subtractive mode and the lower frequency part of the spectrum was cut at $8\,cm^{-1}$. The higher frequency internal modes have been taken at maximal resolution, in additive mode. Spectral width of CCD matrix cell was $650/1024\,cm^{-1}$ for subtractive mode and $220/1024\,cm^{-1}$ for the additive mode. The signal acquisition time was $600\,c$. Spectra were excited with $514.5\,nm$ $500\,mW\,Ar^+$ laser line. Temperature stabilization during acquisition was better then $0.2\,K$.
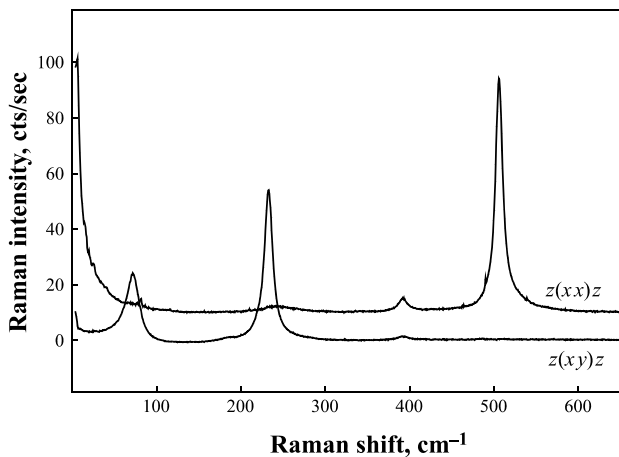

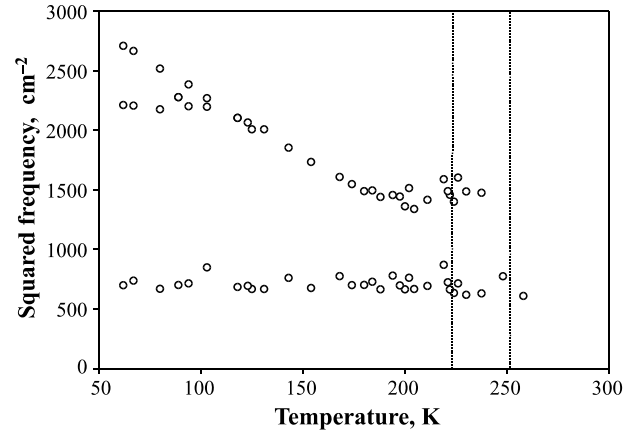Fig. 2. Polarized room temperature Raman spectra of Rb_2KScF_6 crystal.

Results obtained both for room temperature cubic phase and under cooling the crystal down agree well with data of [7] (room temperature spectra are shown in Fig. 2, and Ω^2 versus T dependencies for lower frequency range, in Fig. 3).

Lines obtained at room temperature are well polarized, in accordance with the crystal symmetry, and the positions of the three upper ones agree well with the internal modes of free ScF_6^{3+} ion [11]. Both the lowest mode of the cubic phase and the new low lying lines appearing under cooling may be connected with the vibrations of Rb^+ ions or of ScF_6^{3+} librations.

3. Results of simulations and discussion

Method of lattice dynamics simulations is described in details in Refs. [9,10]. To attribute irreducible representations of crystal symmetry group to the resulting eigenvectors, we use projecting operators approach [12]. These operators P_p were built as:

$$P_p = \frac{d_p}{d_G} \sum_{a \in G} \chi_p^*(a) P_a, \qquad (1)$$

where d_p is the dimension of representation, d_G, the dimension of symmetry group, $\chi_p(a)$, the character of ath irreducible representation of the group G, and P_a, its vibrational representation. Eigenvector of lattice mode f_a corresponds to ath irreducible representation if it satisfies the criterion:

$$\sum_{a \in G} \chi_p^*(a) P_a f_a = \frac{d_G}{d_p} f_a. \qquad (2)$$

This algorithm of eigenvectors attribution was realized within Mathematica 4.2 package.

Calculated and measured frequencies of Raman active lattice vibrations of the cubic phase are given in

Table 1
Calculated and experimental frequencies of lattice modes in the cubic phase (in cm^{-1})

Ir. Rep.	Experiment	Simulation
F_{2g}	89	$26i$
F_{2g}	230	152
E_g	390	342
A_{1g}	505	401

Table 1. The agreement is reasonably good for ab initio simulations of such complex structure. Eigenvectors for F_{1g} and F_{2g} lattice modes are given in Table 2. It is clearly seen from the last table that soft F_{1g} mode in the cubic phase corresponds to the pure librations of ScF_6 octahedra, whereas Raman active hard lattice mode F_{2g} constitutes of a combination of such librations and displacements of Rb^+ ions. This soft mode F_{1g} is the only one that could induce transformation to the tetragonal phase.

Going down, another X_2^+ soft mode should come from the boundary of Brillouin zone, inducing phase transition to the monoclinic phase (see [7,8] for detailed symmetry consideration)—again, only one mode of this symmetry exists in the spectrum. So one can suppose four soft modes (three degenerate components of former F_{1g} and former X_2^+) restoring below T_2. Calculated frequencies and eigenvectors of five lowest modes of the monoclinic phase are given in Table 3. It should be pointed out that the calculated frequencies agree perfectly with the observed lines in Raman spectrum (Fig. 3), and all other calculated values appear well above $60 \, cm^{-1}$, so they can not be considered as "candidates".

Analysis of the calculated eigenvectors show, that all of them include considerable (if not dominating) part of Rb^+ movements, that appears as a result of soft librating modes interaction with hard lattice modes. Being forbidden by crystal symmetry in the higher temperature phases, such interactions become possible after the lattice distortion. As a result, restoring of soft modes bring them into resonant interaction with a hard mode of rubidium displacements (and rather quickly due to big mass of Rb^+ and low frequency of such a mode). And this interaction complicates the usual behavior of restoring soft modes.

Table 2
Examples of eigenvectors for lattice modes of the cubic phase

		Rb	Rb	K	Sc	F	F	F	F	F	F
$F_{2g}26i$ cm^{-1}	x	0.35	−0.35	0	0	−0.16	0.16	0	0	0.05	−0.05
	y	−0.52	0.52	0	0	0.10	−0.10	−0.05	0.05	0	0
	z	0.18	−0.18	0	0	0	0	0.16	−0.16	0.10	−0.10
$F_{1g}66i$ cm^{-1}	x	0	0	0	0	0.39	−0.39	0	0	0.31	−0.31
	y	0	0	0	0	0.08	−0.08	0.31	−0.31	0	0
	z	0	0	0	0	0	0	0.39	−0.39	0.08	−0.08

Table 3
Eigenvectors for lowest lattice modes of the monoclinic phase

		Rb	Rb	Rb	Rb	K	K	Sc	Sc	F	F	F	F	F	F	F	F	F	F	F	F
22 cm^{-1}	x	−0.1	0.1	0.1	0.1	0.0	0.0	0.0	0.0	0.0	−0.1	0.1	0.0	−0.1	0.1	0.0	0.1	−0.1	0.0	0.1	−0.1
	y	0.3	0.3	0.2	−0.2	0.0	0.0	0.0	0.0	0.1	−0.1	0.1	−0.1	0.1	−0.1	0.1	−0.1	0.1	−0.1	0.1	−0.1
	z	0.3	0.3	0.4	−0.4	0.0	0.0	0.0	0.0	0.0	−0.1	−0.1	0.0	−0.1	−0.1	0.0	0.1	0.1	0.0	0.1	0.1
29 cm^{-1}	x	0.0	0.0	0.1	−0.1	0.0	0.0	0.0	0.0	0.0	−0.1	0.0	0.0	0.1	−0.1	0.0	0.0	0.0	0.0	0.0	−0.1
	y	−0.4	−0.3	0.6	0.4	0.0	0.0	0.0	0.0	0.1	−0.1	0.0	0.1	−0.1	0.0	−0.1	0.0	−0.1	−0.2	0.0	−0.1
	z	0.0	0.0	−0.1	0.0	0.0	0.0	0.0	0.0	0.0	0.1	0.0	0.0	0.0	0.1	0.0	0.1	0.0	0.0	0.0	0.1
31 cm^{-1}	x	0.4	0.4	−0.4	−0.4	0.0	0.0	0.0	0.0	0.0	−0.1	−0.1	0.0	−0.1	−0.1	0.0	0.1	0.1	0.0	0.1	0.1
	y	−0.1	0.1	−0.1	0.1	0.0	0.0	0.0	0.0	0.0	−0.1	−0.1	0.0	0.1	0.1	0.0	−0.1	−0.1	0.0	0.1	0.1
	z	0.1	0.1	−0.1	−0.1	0.0	0.0	0.0	0.0	0.0	−0.2	0.1	0.0	−0.2	0.1	0.0	0.2	−0.1	0.0	0.2	−0.1
37 cm^{-1}	x	−0.1	−0.1	0.2	0.1	0.0	0.0	0.0	0.0	0.0	0.0	0.1	0.0	0.0	0.1	0.0	0.0	−0.1	0.0	0.0	−0.1
	y	−0.4	0.4	−0.4	0.4	0.0	0.0	0.0	0.0	−0.1	0.0	0.1	0.1	0.0	−0.1	−0.1	0.0	0.1	0.1	0.0	−0.1
	z	0.2	0.2	−0.2	−0.2	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
43 cm^{-1}	x	−0.4	0.4	−0.5	0.5	0.0	0.0	0.0	0.0	−0.1	0.0	0.0	0.1	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
	y	0.0	0.0	0.0	0.1	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	−0.1	0.0	0.0	0.0	0.0
	z	0.0	0.1	0.1	−0.1	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	−0.1	0.0	0.0

4. Conclusion

Using a symmetry approach we have attributed the calculated eigenvectors of crystal lattice vibrations to the lines of experimental Raman spectra of Rb_2KScF_6 crystal. The obtained information on soft mode eigenvectors (observed in the experimental spectrum) allow to ascribe microscopic mechanism of lattice instability to rotations of ScF_6 groups and to explain unusual complex behavior of the temperature dependence of these modes by their interaction with hard mode displacements of Rb^+ ions below phase transition.

Acknowledgements

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