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Hydrostatic Pressure-Induced Phase Transitions in Rb_2KInF_6 and Rb_2KScF_6 Crystals: Raman Spectra and Lattice Dynamics Simulations

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Raman scattering spectra of Rb_2KInF_6 and Rb_2KScF_6 crystals have been studied under hydrostatic pressure up to 5.3 GPa at room temperature. Results are interpreted within semiempirical simulations of the lattice dynamics. Observed phase transitions both in Rb_2KInF_6 and Rb_2KScF_6 crystals are associated with condensation of soft F_{1g} phonon mode. High-pressure phases for both crystals are supposed to be of C2/m space group.

Keywords Rb_2KInF_6; Rb_2KScF_6; phase transitions; Raman scattering; lattice dynamics

I. Introduction

The Rb_2KInF_6 and Rb_2KScF_6 crystals belong to the perovskite-like crystals with the elpasolite structure $A_2B(^1)B(^2)X_6$ (A and B are metal cations or more complex molecular ions and X are oxygen or halogen anions, high symmetry phase space group $Fm3m$, $Z = 4$), which are extensively studied due to their wide variety of distorted structures and exciting complex sequences of phase transitions [1]. Structural phase transitions in the elpasolites are usually connected with lattice instability to BX_6 octahedrons rotations due to soft phonons condensation [1, 2].

Vibrational representation of the cubic phase group at Brillouin zone center is:

$$\Gamma_{\text{vibr}}(Fm3m) = A_{1g}(xx,\ yy,\ zz) + E_g(xx,\ yy,\ zz) + 2F_{2g}(xz,\ yz,\ xy) + F_{1g} + 5E_{1u} + F_{2u}. \quad (1)$$

where corresponding components of the Raman scattering tensor are given in brackets.

Site symmetry of BX_6 ions coincides with the free ion symmetry; symmetry and frequencies of the free ion vibrations are: $\nu_1(A_{1g})$ – 497 cm^{-1}, $\nu_2(E_g)$ – 395 cm^{-1}, $\nu_3(F_{1u})$ – 447 cm^{-1}, $\nu_4(F_{1u})$ – 226 cm^{-1}, $\nu_5(F_{2g})$ – 229 cm^{-1}, $\nu_6(F_{2u})$ – 162 cm^{-1} for InF_6 and 495 cm^{-1}, $\nu_2(E_g)$ – 375 cm^{-1}, $\nu_3(F_{1u})$ – 458 cm^{-1}, $\nu_4(F_{1u})$ – 257 cm^{-1}, $\nu_5(F_{2g})$ – 235 cm^{-1},

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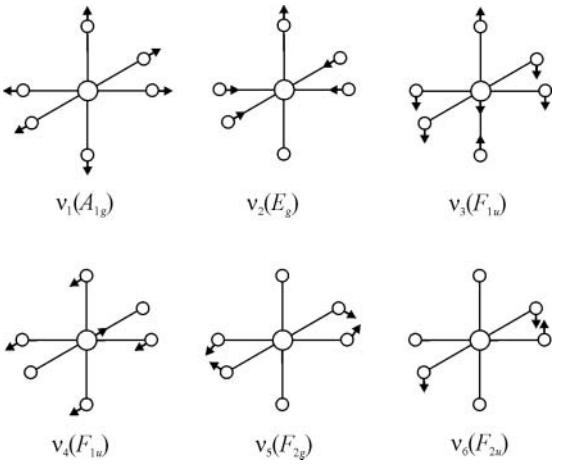

Figure 1. Normal modes of vibration of octahedral BX_6 molecules.

$\nu_6(F_{2u})$ – unknown for ScF_6 [3]. Normal modes of vibration of octahedral BX_6 molecules are given in Fig. 1.

Experimental Raman spectra of Rb_2KScF_6 at high pressure have been investigated earlier in Ref. [4]. Experimental Raman spectra and lattice dynamics calculation within "rigid" ion model for Rb_2KInF_6 have been studied in Ref. [5]. The aim of this paper is to investigate Raman spectra of Rb_2KInF_6 and Rb_2KScF_6 crystals under hydrostatic pressure looking for possible phase transitions and understanding their mechanisms.

II. Experimental Technique and Raman Spectra

Samples for experiments were optically transparent [6] and without colored defects or inclusions visible under the microscope, with a diameter of 9–10 mm and length of 10-15 mm. The X-ray powder diffraction analysis confirmed the absence of extra phase inclusions for both crystals. High pressure experiments were performed with diamond anvil cell similar to Ref. [7] at room temperature. The diameter of the cavity with the sample was 0.25 mm, and its height was 0.1 mm. Pressure was measured within 0.05 GPa accuracy by ruby luminescence line shift; ruby microcrystal was placed in the cell near unoriented microcrystal under study. The pressure transmitting medium was a well dehydrated mixture of ethanol and methanol. Back scattering Raman spectra have been obtained with T-64000 (Horiba – Jobin Yvon) triple spectrometer with matrix registration and Ar^+ (514,5 nm) excitation.

Lines at 507, 379, and 218 cm^{-1} correspond to internal InF_6 modes (ν_1, ν_2, ν_5, respectively), and lines at 505, 390, and 230 cm^{-1} correspond to internal ScF_6 modes (ν_1, ν_2, ν_5, respectively). Frequency of the only Raman active lattice mode is 69 cm^{-1} for Rb_2KInF_6 and 89 cm^{-1} for Rb_2KScF_6 at 295 K. The Raman spectra in the pressure range up to 0.9 GPa for Rb_2KInF_6 and to 1.0 GPa for Rb_2KScF_6 are typical for cubic phases of these crystals [4, 5]. At higher pressures, the additional lines become visible in the spectra. Transformation of the higher frequency part of the spectrum is given in Fig. 2. It should be noted that higher frequency part of these spectra corresponds to nondegenerated ν_1 internal modes of $B(^2)F_6$ groups. Appearance of these extra lines here should be associated with increasing of primitive cell volume of the cubic phase.

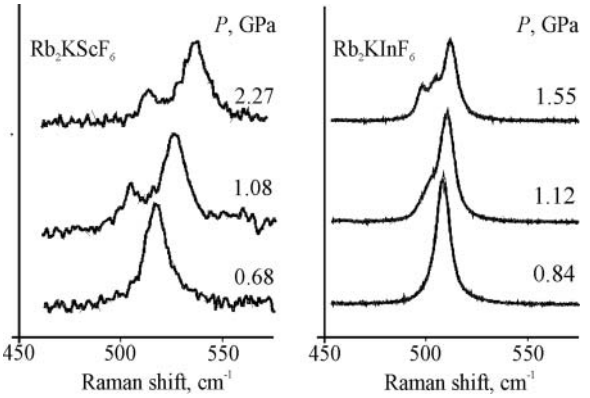

Figure 2. Pressure transformation of the high frequency part of the spectrum (A_{1g} internal mode).

III. Computational Details and Comparison with Experiments

In order to calculate lattice vibrations of crystals, LADY program package [8] was used. As the first step dynamics of free $B^{(2)}F_6$ groups was simulated; experimental data [3] were used as a reference. The best agreement between experimental values of atomic vibrations with the calculated values was obtained using the so-called "hybrid model" [9]. This model is a combination of valence force field (VFF) and "rigid-ion" models (RIM). Then we have simulated complete spectra of the crystals; interionic interactions between Rb–F and K–F have been described in the fairly common model of "rigid-ion", where interatomic potential is considered as a sum of long range Coulomb electrostatic:

$$V(r_{ij}) = \tfrac{1}{2}\sum_{i,j}\frac{Z_i Z_j}{r_{ij}} + U(r_{ij}) \tag{2}$$

and short range Born–Mayer potentials:

$$U(r_{ij}) = \lambda \exp(-r_{ij}/\rho) \tag{3}$$

where r_{ij} – interatomic distance, λ, ρ – parameters characterizing the ion pair interaction.

To obtain a satisfactory agreement of experimental and calculated results interactions within the octahedral groups BX_6 in crystals (interaction between In–F, Sc–F, and F–F) potential function was composed as a sum of rigid-ion potential and the VFF potential. VFF model is applicable in describing the lattice dynamics of covalent, ionic, and ionic-molecular crystals. Free ions have been described in the framework of the VFF model only.

Thus, for lattice dynamics calculations of crystals the potential function takes the form:

$$V(r_{ij}) = \tfrac{1}{2}\sum_{i,j}\frac{Z_i Z_j}{r_{ij}} + U(r_{ij}) + U_{VFF} \tag{4}$$

In order to find λ and ρ parameters of the model, an optimization program was written. Initial values of parameters were set at random within the ranges typical for the perovskite-like fluorides. Experimental data on crystal structures [6, 10] at room temperature and zero pressure were used, and lattice stability conditions were taken into account. Resulting

Table 1
Comparison of calculated and experimental vibrational frequencies for Rb_2KInF_6 and Rb_2KScF_6 crystals and InF_6 and ScF_6 free molecular groups (cm^{-1}).

	source	A_{1g}	E_g	F_{2g}	F_{2g}	F_{1u}	F_{1u}	F_{1u}	F_{1u}	F_{1u}	F_{2u}	F_{1g}
Rb_2KInF_6	Exp.	507	379	218	69	–	–	–	–	–	–	–
	Calc	509	375	219	63	461	172	153	68	0	48	9
InF_6	[3]	497	395	229	–	447	226	–	–	–	162	–
	Calc.	495	395	229	–	443	226	–	–	–	162	180
Rb_2KScF_6	Exp.	505	390	230	73	–	–	–	–	–	–	–
	Calc.	505	390	230	73	481	255	154	74	0	136	10
ScF_6	[3]	495	375	235	–	458	257	–	–	–	–	–
	Calc.	495	375	235	–	458	257				254	184

model parameters were obtained by minimization of residual values of the simulated and experimental Raman frequencies of the cubic phases using the Fletcher-Reeves method. In the case of suspension of the Fletcher-Reeves method because of the incompatible model parameters, initial parameters of the model were set randomly again. Comparison of calculated and experimental spectra for Rb_2KInF_6 and Rb_2KScF_6 crystals, as well as InF_6 and ScF_6 free molecular groups, is shown in Table 1. Brillouin zone investigation for both crystals has been performed. Lattice instability associated with the triply degenerated F_{1g} soft phonon mode has been found. That soft mode is associated with displacements of four fluorine atoms from $B^{(2)}F_6$ octahedrons only and corresponds to the rotation of the octahedron as a whole around four-hold axis. Dependences of F_{1g} mode frequency vs pressure for Rb_2KInF_6 and Rb_2KScF_6 crystals are shown in Fig. 3.

It is clear from this picture that frequency of this mode in both crystals decreases under compression and comes to condensation at 0.9 GPa for Rb_2KInF_6 and at 1.0 GPa for Rb_2KScF_6, which corresponds to observed phase transition points. Above these points crystal structures become unstable with respect to these displacements. Due to degeneration of this mode, several distorted high-pressure phases are possible, namely: *I*4/*m*, *R*3, *C*2/*m*, and *P*1 [5]. Simulation of lattice dynamics of these phases with the same interatomic

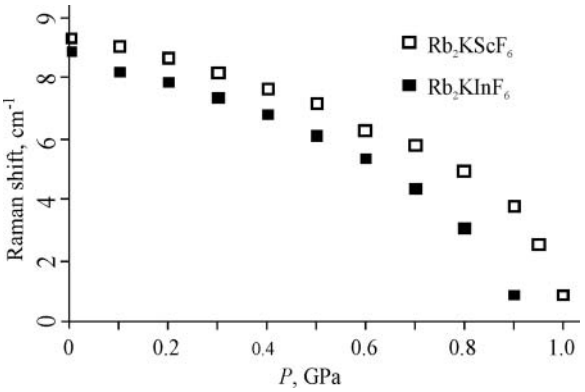

Figure 3. Pressure dependences of soft phonon mode frequency.

potential as compared with experimental spectra shows that the most probable high-pressure phase is of $C2/m$ space group for both crystals studied.

IV. Conclusion

Experimental measurements of Raman spectra of Rb_2KInF_6 and Rb_2KScF_6 crystals under high hydrostatic pressure have been made. To interpret the results, semi-empirical model of their lattice dynamics has been built that agrees quantitatively with both experimental spectra of the crystals and free octahedral ions. Investigations of the model show that lattice instabilities found at 0.9 GPa for Rb_2KInF_6 and at 1.0 GPa for Rb_2KScF_6 are induced by soft phonon mode condensation. For both crystals the most probable resulting high-pressure phase is of $C2/m$ space group.

Acknowledgments

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