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Raman Scattering Study Temperature Phase Transitions of Rb_2KInF_6 Crystal

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Raman scattering spectra of Rb_2KInF_6 crystal have been studied in a wide temperature range, including two phase transitions: from cubic to tetragonal, and then – to the monoclinic phase. Hardening of soft phonon modes was observed that attributes them to the transitions of displacive type. Parameters of Raman lines have been quantitatively analyzed and found in good agreement with known thermodynamic characteristics of these transitions. No evidences of order – disorder processes were observed in the Raman spectra of the high-symmetry phase.

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

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1. Introduction

Elpasolite crystal of Rb_2KInF_6 is a member of the perovskite-like family (high symmetry phase G_0, space group $Fm3m$, $Z = 4$), that are extensively studied for their wide variety of structures and exciting complex sequences of phase transitions [1]. Structural phase transitions in the elpasolites are usually connected with lattice instability to CX_6 octahedrons rotations due to soft phonons condensation[1, 2]. Transitions temperatures Rb_2KInF_6 crystal are $T_1 = 283$ K (into G_1 phase, space group $I114/m$, $Z = 2$) and $T_2 = 264$ K (into G_2 phase, space group $P12_1/n1$, $Z = 2$) [3]. *Ab initio* simulations of lattice stability and dynamics for transition from Fm–$3m$ into $I114/m$ phase of this crystal have shown [4] that soft mode condensation could induce these phase transformations. Therefore we've performed this detailed investigation of Raman spectra of Rb_2KInF_6 crystal. Vibrational representation of the cubic phase group at Brillouin zone center is:

$$\Gamma_{vibr}(Fm-3m) = A_{1g}(xx, yy, zz)+E_g(xx, yy, zz)+2F_{2g}(xz, yz, xy)+F_{1g}+5E_{1u}+F_{2u}, \quad (1)$$

where corresponding components of the Raman scattering tensor are given in brackets. In the tetragonal phase, the reduction of the oscillation representation at the center of the

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Brillouin zone has the form

$$\Gamma_{vibr}(I114/m) = 3A_g(xx, yy, zz) + 3B_g(xx, yy, xy) + 3E_g(xz, yz) + 5A_u + 6E_u + B_u \quad (2)$$

In the monoclinic phase, the reduction of the oscillation representation of the symmetry group has the form

$$\Gamma_{vibr}(P12_1/n1) = 12A_g(xx, yy, zz, xy, yx) + 12B_g(xz, yz, zx, zy) + 18A_u + 18B_u \quad (3)$$

The transition to the monoclinic phase is accompanied by doubling of the unit cell volume. The modes at the X (0, 0, π/a) point at the Brillouin zone, including the possible soft mode, are Raman-inactive; however, they can become Raman-active below the second transition point (and the soft mode can also be recovered there). We might also expect further splitting of the modes that are degenerate in the tetragonal phase, including the recovering soft mode corresponding to the transition from the cubic to the tetragonal phase. First order transformation to G_2 phase corresponds to $X_2{}^+$ irreducible representation of G_0 phase or $Z_2{}^+$ of G_1 phase; and doubles unit cell volume. Site symmetry of InF_6 ions coincides with the free ion symmetry; symmetry and frequencies of the free ion vibrations are [5]: $\nu_1(A_{1g})$ – 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}.

So the aim of this paper is to perform investigation of Raman spectra of Rb_2KInF_6 crystal in a wide temperature range, to study the mechanism of these phase transitions.

2. Experimental Technique and Results

Samples for experiments were optically transparent [6] and without colored defects or inclusions visible under the microscope. Spectra in the geometry of 180° were obtained with T-64000 Raman spectrometer (Horiba Jobin Yvon) in 10 to 1200 cm^{-1} frequency range. Spectra were excited with 514.5 nm Ar^+ laser. Temperature stabilization during spectra acquisition – better then 0.2 K. Lines at 504, 379 and 218 cm^{-1} correspond to internal InF_6 modes (ν_1, ν_2, ν_5 respectively). Frequency of the only Raman active lattice mode is 69 cm^{-1} at 295 K. Transformation of the lower frequency part of the spectrum (that corresponds to lattice vibrations) is given in Fig. 1. It could be subdivided in two parts: below and above 54 cm^{-1}. Higher frequency part includes hard lattice modes. Here we observe slow high frequency shift of 69 cm^{-1} lattice mode mentioned above, that splits in two below T_1 transition point; next transition at T_2 results in its further splitting and deeper cooling gives rise for extra weaker lines appearance.

In the lowest (<60 cm^{-1}) part of the spectra we've observed growth and widening of the central peak wing under cooling just above the upper transition point. Below T_1 this wide wing may be interpreted as an appearance of a low frequency weak wide band, where some maxima (at 36 cm^{-1}, 42 cm^{-1} and 46 cm^{-1}) may be marked out. Positions of the lowest maxima (before 44 cm^{-1}) stay about constant on cooling as well. Their intensities decrease slowly, and they can be hardly seen above background level. According to selection rules both soft modes in higher symmetry phases correspond to InF_6 groups rotations without their distortions or admixing of other degrees of freedom – there are no other vibrations of the same symmetry in the crystals spectrum. However below the second transition symmetry allows for such interaction with rubidium ions displacements, that could be mixed up to eigenvectors of restoring modes. Temperature evolution of ν_1 internal mode is shown in Fig. 2.

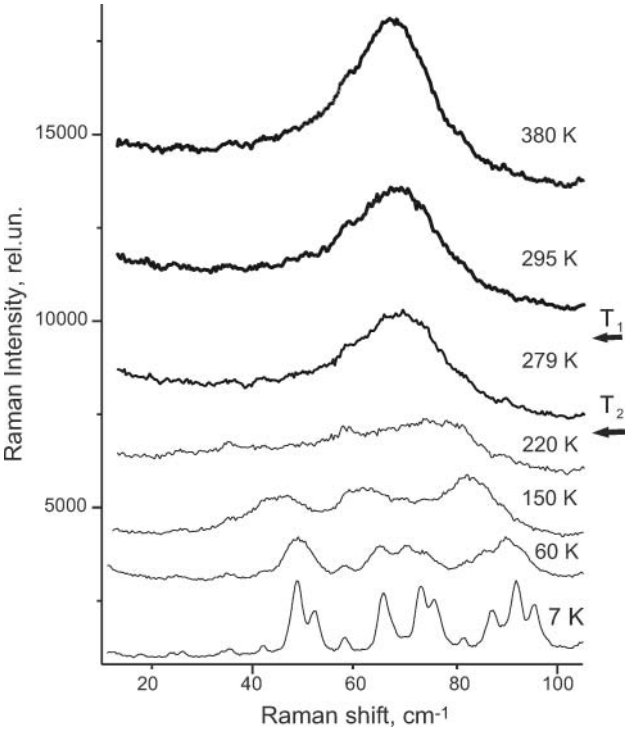

Figure 1. Temperature transformation of low frequency lattice modes spectrum. The arrows indicate the phase transitions.

New line appearance at lower temperature, that agrees with selection rules. As before, this line coming from Brillouin zone boundary becomes visible somewhere below transition point. Extrapolation of this dependence in the cubic phase with the function [7, 8]:

$$\Omega_\alpha(T) = \Omega_\alpha(0)\exp(-3\gamma_\alpha a T) \tag{4}$$

and temperature dependence of these lines positions is given in Fig. 3. The product of Grunizen parameter by temperature expansion coefficient $\gamma_\alpha a \approx 1.5\times10^{-4}$ K^{-1}. Extrapolated to $T = 0$ frequency equals 514 cm^{-1}. Obtained value of Grunizen parameter shows extremely weak anharmonicity of this vibration.

Transition to the tetragonal phase changes considerably temperature dependence of this mode as well. The frequency shift from the dependence, extrapolated in the cubic phase, is shown in Fig. 4.

Slight deviation from extrapolated value appears in the tetragonal phase of Rb_2KInF_6 crystal only, in contrast to Rb_2KScF_6 crystal, where such deviation from extrapolated value was observed in a rather wide (about 50 K) pretransitional region of the cubic phase [9]. This deviation grows in the tetragonal phase of Rb_2KInF_6 and increases almost linearly under cooling in the monoclinic one, that corresponds to the phase transition of the second order or close to second order.

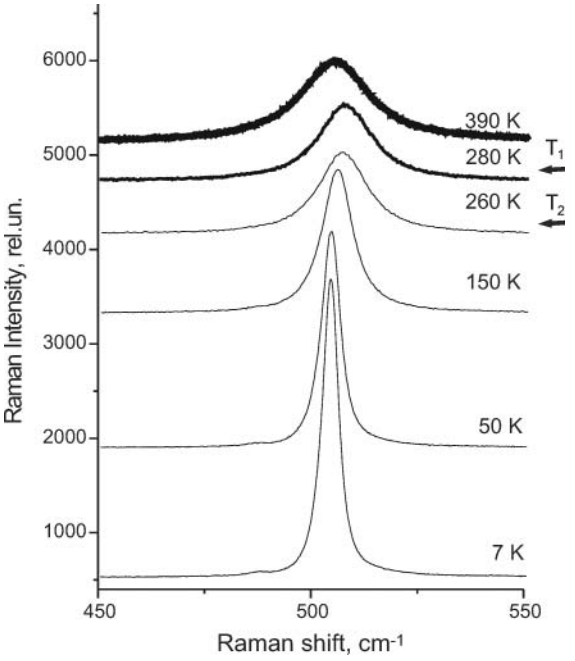

Figure 2. Temperature transformation of the spectrum near $\nu_1(A_{1g})$ internal mode. The arrows indicate the phase transitions.

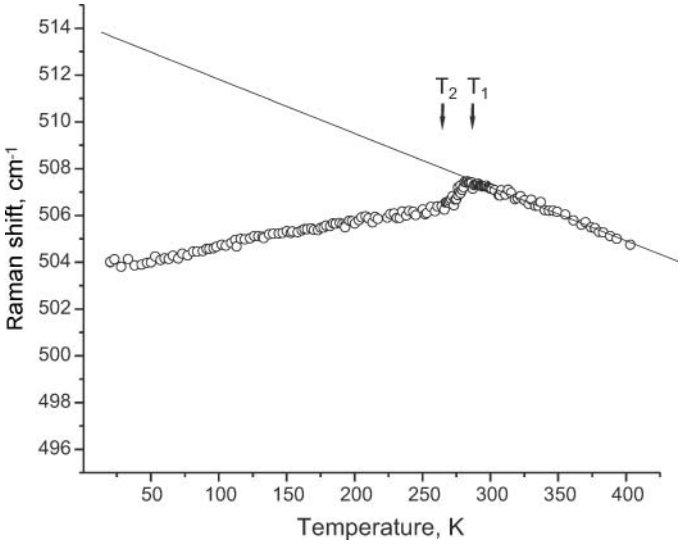

Figure 3. Temperature dependence of ν_1 internal modes positions. The arrows point to the phase transitions temperatures: $T_1 = 283$ K, $T_2 = 264$ K.

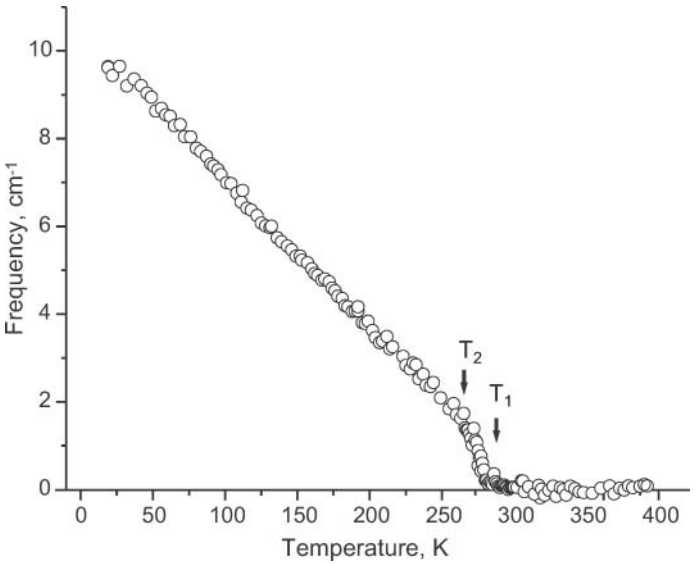

Figure 4. Temperature dependence of ν_1 (A_{1g}) internal mode shift from it's extrapolated value. The arrows point to the phase transitions temperatures: $T_1 = 283$ K, $T_2 = 264$ K.

5. Conclusion

As a result of these investigations we can conclude, that phase transitions in Rb_2KInF_6 crystals are accompanied with soft modes restorations; that attributes them to displacive phase transitions. According to group theory analysis eigenvectors of both soft modes are connected with rotations of InF_6^+ ions, though below G_1–G_2 transition these modes could be mixed with other degrees of freedom – in particular, with rubidium ions displacements. Anomalous dependences of parameters of hard lattice and internal modes have been found and interpreted; their quantitative analysis confirms attribution of G_0–G_1 transition to the second order, and G_1–G_2 one—to the second order. Small values of lines widths and their temperature dependences confirm that phonon damping in the higher symmetry phase is connected with phonon decays due to their anharmonicity but not to some lattice disordering.

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