

LATTICE DYNAMICS AND PHASE TRANSITIONS

Soft-Mode Condensation in Raman Spectra of the Rb_2KScF_6 Elpasolite

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Abstract—This paper reports on the first observation of soft-mode condensation in the Raman spectra of the Rb_2KScF_6 elpasolite crystal below the transition points from the cubic to tetragonal and, subsequently, monoclinic phase. © 2001 MAIK “Nauka/Interperiodica”.

1. INTRODUCTION

The A_2BCX_6 elpasolites (high-symmetry phase G_0 , space group $Fm\bar{3}m$, $Z = 4$), a family of perovskite-like crystals, are subjects of considerable interest because of their application potential and as model media to study phase-transition mechanisms [1]. Phase transitions (PT) in these structures are usually associated with the lattice becoming unstable to rotation of the CX_6 octahedral ions, which is caused by phonon-mode condensation. Soft mode condensation has been successfully observed before only in bromine-, chlorine-, and oxygen-containing elpasolites [2–5]. Studies of transitions in the fluorine compounds of this family performed, in particular, using vibrational spectroscopy are usually rendered difficult by their comparatively high temperatures. The Rb_2KScF_6 crystal appears a promising system from this standpoint. Indeed, its phase transition temperatures are relatively low: $T_1 = 252$ K (to the G_1 phase, space group $I114/m$, $Z = 2$) and $T_2 = 223$ K (to the G_2 phase, space group $P112_1/n$, $Z = 2$) [6]. This suggests that one could obtain spectra with narrow lines and a low background. A recent first-principles calculation of the stability and dynamics of the Rb_2KScF_6 lattice [7] showed that the phase transitions observed to occur in this crystal can also be due to soft phonon-mode condensation. Earlier studies of Raman scattering (RS) spectra did not, however, provide experimental support of this conjecture [8], just as in the case of other fluorine-containing elpasolites isomorphous with respect to Rb_2KScF_6 [9]. This stimulated the present study of the low-frequency Raman spectrum of the Rb_2KScF_6 crystal as a search for soft phonon modes.

2. CRYSTAL STRUCTURE AND NORMAL-MODE SYMMETRY

Figure 1 presents schematically the unit cell of the high-symmetry phase G_0 . The vibrational representa-

tion can be reduced into irreducible representations (IR) at the Brillouin zone center as

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

where the parentheses contain the RS tensor components to which the corresponding vibrations contribute. The table identifies the atoms involved in these vibrations. The position symmetry of the ScF_6 group in the structure coincides with that of the free group, and the symmetries, types, and frequencies of its Raman-active normal vibrations taken from [10] are given in Fig. 2. Figure 3 displays the correlation diagram of the vibrations active in the RS spectra of the cubic and tetragonal phases. As follows from this diagram, only one lattice vibration mode (hard) is active in the spectrum of the cubic phase (the others being internal vibrations of the ScF_6 groups), but the soft mode hardening (which splits below the transition in two) can be seen in RS below the transition point.

Vibrational representation of the group symmetry of the Rb_2KScF_6 cubic phase

IR	A_{1g} (xx, yy, zz)	E_g (xx, yy, zz)	F_{1g}	F_{2g} (xz, yz, xy)	F_{1u}	F_{2u}
2Rb	–	–	–	1	1	–
K	–	–	–	–	1	–
Sc	–	–	–	–	1	–
6F	1	1	1	1	2	1
Γ_{vib}	1	1	1	2	5	1

Note: F_{1g} is the representation corresponding to the cubic-phase soft-mode symmetry.

The transition to the G_2 phase occurs according to the X_5^+ representation of the G_0 phase (which corresponds to the Z_5^+ representation of the G_1 phase; we use here the notation of [9]) and is accompanied by primitive-cell doubling. The modes corresponding to the $X(Z)$ point in the Brillouin zone are Raman inactive; however, as can be seen from the correlation diagram in Fig. 4, they may also be observed below the second transition point.

3. EXPERIMENT

The samples for the experiment, measuring $2 \times 2 \times 4$ mm, were chosen from the same crystallization as in [6] and were cut such that, in the G_0 phase, their edges were aligned with the crystallographic axes (note that, after the phase transitions, a well-developed domain structure precluding measurement of polarized spectra in the low-temperature phases is formed). The crystals were optically transparent and did not contain colored defects or inclusions visible under a microscope. The spectra were obtained on a Jobin-Yvon T-64000 Raman spectrometer with CCD-array detection. To suppress the elastic scattering wing as much as possible, a triple-monochromator mode was used with subtraction of dispersion and with a low-frequency cutoff at 8 cm^{-1} . The spectral width of the slits was 1 cm^{-1} , the spectral size of the array cell was $650/1024 \text{ cm}^{-1}$, and the signal accumulation time was 600 s. The excitation was accomplished with 514.5 nm polarized radiation from a 500 mW Ar^+ laser. The sample temperature during spectral measurement was stabilized to no worse than 0.2 K .

4. RESULTS AND DISCUSSION

The number and polarization of the spectral lines detected in the high-temperature cubic phase far from the transition point agree well with calculations and earlier observations [8, 9]. The frequency of the only Raman-active lattice vibration mode at room temperature is 89 cm^{-1} , and it increases slightly under cooling; thus, it does not interfere with the observation of anomalies in the low-frequency part of the spectrum.

As the temperature is lowered, one observes the central scattering peak to grow in intensity and broaden a few degrees before the transition point. Below T_1 , a broad wing appears near the central peak, which can be interpreted as an enhancement of a low-intensity broad band (Fig. 5); at lower temperatures, one can discriminate two maxima in it, at 26 and 39 cm^{-1} . Figure 6 shows the temperature dependence of the squared frequencies of the line maxima (the parameters of the overlapping profiles were derived with the SigmaPlot 5.0 program with a dispersive function used for line contours). No noticeable frequency shifts of these lines are observed to occur in the tetragonal phase (because of the background level being comparable to the line

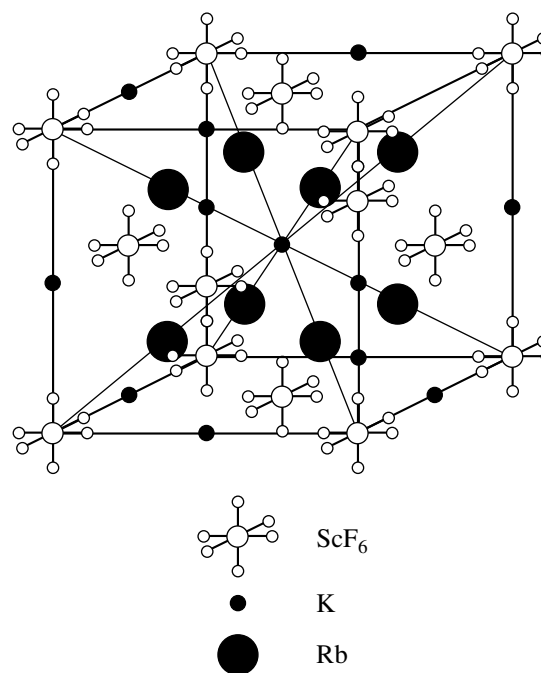


Fig. 1. Structure of the original phase G_0 of the Rb_2KScF_6 crystal.

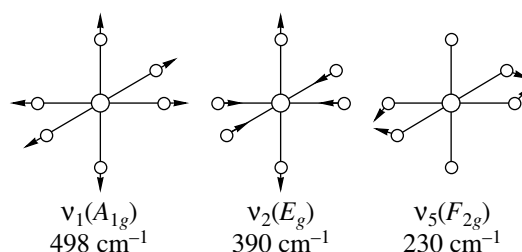


Fig. 2. Types of Raman-active normal modes of the ScF_6 group.

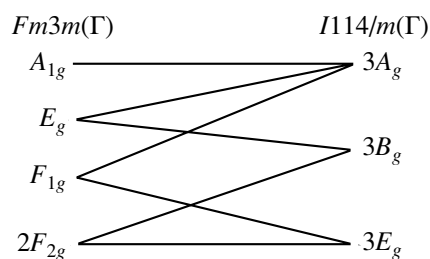


Fig. 3. Correlation diagram of the Raman-active modes of the cubic and tetragonal phases.

intensity, the line position could not be determined with a sufficiently high accuracy); one can only notice a certain redistribution of the intensity to higher frequencies within this band with decreasing temperature and a lowering of the central peak intensity, which is possibly caused by rearrangement of the domain structure.

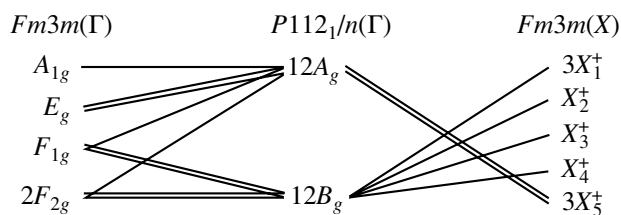


Fig. 4. Correlation diagram of the Raman-active modes of the cubic and monoclinic phases.

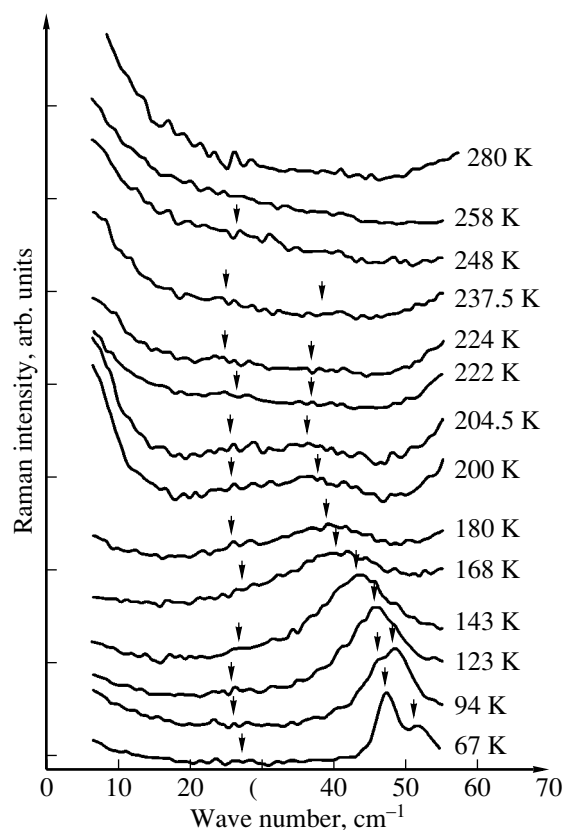


Fig. 5. Temperature-induced changes in the low-frequency part of the Rb_2KScF_6 spectrum.

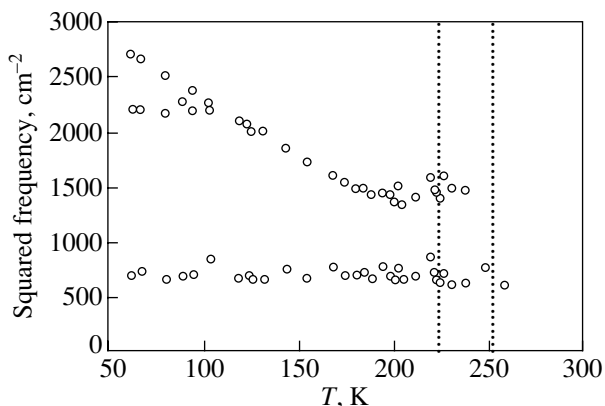


Fig. 6. Temperature dependence of the squared frequencies of the observed low-frequency lines.

As the second transition point is reached, the elastic scattering intensity increases in a jump and the band undergoes an intensity redistribution, with its high-frequency part growing noticeably. The frequency of this maximum increases monotonically under cooling. The temperature dependence of the squared frequency is close to being a linear dependence; this is a feature characteristic of soft modes associated with displacive phase transitions, either of the second order or of the first close to the second order. Below 100 K, where the line widths become smaller because of the decrease in anharmonicity, the corresponding band splits in two components. As the temperature is lowered still more, the high-frequency component of the doublet thus formed continues to move up, while the low-frequency one remains unchanged ($47\text{--}48\text{ cm}^{-1}$).

The lowest frequency maximum also remains practically in the same position ($26\text{--}27\text{ cm}^{-1}$). Its intensity falls off slowly, until it becomes practically indistinguishable against the background noise below 100 K.

Thus, one may conclude that the phase transformations in Rb_2KScF_6 studied here are accompanied by soft phonon-mode condensation; hence, they should be assigned to displacive transitions. As shown in using group-theoretical analysis, the first phase transition is associated with a rotation of the ScF_6^+ octahedral molecular ions (table), whereas the second one may be induced by a more complex deformation involving both rotation of these ions and cation displacement [8, 9]. At the same time, the first transition is accompanied by considerable pretransition effects and the lines forming below the transition point exhibit extremely low intensities and large widths, which may be caused by either strong order-parameter fluctuations over a broad enough temperature interval or by the onset of structural disorder in the pretransition region [11].

Because all critical vibrations in the low-temperature phase belong to one totally symmetric representation, their closeness in position and the strong temperature dependence of their frequencies must inevitably give rise to strong coupling and, hence, mixing of various types of vibrations. Thus, even if these strong fluctuation effects are originally related to the cubic-to-tetragonal phase transition, the interaction between the critical vibrations should also cause intense fluctuations of the order parameter governing the second transition. Only a substantial decrease in temperature weakens this coupling and permits reliable observation of the recovery of the corresponding modes.

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