RAMAN SPECTRA AND PHASE TRANSITIONS IN THE Rb_2KScF_6 ELPASOLITE

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Phase transitions in A_2BCX_6 elpasolites (high-symmetry phase G_0, space group $Fm3m$, $Z = 4$) 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 in bromine-, chlorine-, and oxygen-containing elpasolites; the Rb_2KScF_6 crystal appears a promising fluorine-based system from such investigations. Its 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 $G2$ phase, space group $P112_1/n$, $Z = 2$) [1], that suggests a possibility to 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 [2] showed that the phase transitions observed in this crystal can also be due to soft phonon condensation. Earlier studies of Raman scattering spectra did not, however, provide experimental support of this [3], just as in the case of other fluorine-containing elpasolites [4]. This stimulated the present study of the Rb_2KScF_6 crystal.

The number and polarization of the spectral lines detected in the high-temperature cubic phase far from the transition point agree well with symmetry analysis and earlier observations [3–5]). Cooling the crystal down broadens the central peak a few kelvins above the T_1 point. Some pretransitional effects were detected: normal frequency growth under cooling becomes slower, and a leakage of line intensities between Raman tensor components takes place. Below T_1 splitting of ScF_6 internal vibrations was observed, in accordance with their site symmetry, while the temperature behavior of the line parameters changes noticeably. A broad wing appears near the central peak, which can be interpreted as an appearance of a low-intensity broad band; at lower temperatures it can be discriminated into two maxima, at 26 and 39 cm^{-1}. No noticeable frequency shifts of these lines are observed in G_1 phase.

As the T_2 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. The frequency of this maximum increases linearly under further cooling dependence; that is typical for soft modes associated with displacive phase transitions. Below 100K this band splits into 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 (~48 cm^{-1}). The lowest frequency maximum also remains practically in the same position (26–27 cm^{-1}). Its intensity falls off slowly, until it becomes hardly distinguishable against the background noise below 100K.

Thus studied transitions in Rb_2KScF_6 are accompanied by soft phonon-mode condensations and should be assigned to the displacive type. Still the first transition is accompanied by considerable pretransition effects and the lines forming below it exhibit extremely low intensities and large widths, which may be caused by either strong order-parameter fluctuations over a broad temperature interval or by the onset of structural disorder in the pretransition region [6].

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