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EFFECT OF TETRAGONAL–TETRAGONAL PHASE TRANSITION ON RAMAN SPECTRA AND LATTICE DYNAMICS OF $CsScF_4$ CRYSTAL

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Raman scattering spectra of $CsScF_4$ crystal has been studied in both tetragonal phases, and lattice dynamics of the upper phase has been simulated numerically. Soft mode condensation at Brillouin zone boundary was obtained in the model simulations, and observed in experimental spectra below the tetragonal–tetragonal phase transition.

Keywords: Raman spectra; $CsScF_4$; lattice dynamics; soft mode

INTRODUCTION

Crystal of $CsScF_4$ presents a typical example of layered perovskite structure. According to X-ray data and macroscopic measurements,[1] at higher temperatures it has D_{4h}^1 lattice formed by square layers of ScF_6 octahedrons connected *via* common F atoms, and separated with Cs^+ ions in interlayer holes (Fig. 1). Cooling below 475 K results in phase transition to D_{4h}^5 phase with elementary cell of doubled volume, and further cooling down 317 K – in next transition (ferroelastic) to D_{2h}^{13} phase with further doubling of the cell volume. (This temperature of upper phase transition differ slightly from the one obtained in this study; such variations has been pointed out in Ref. [1] also). This phase sequence is rather unusual for Cs-containing perovskites,[2, 3] and seems closer to the one observed in $RbAlF_4$, were lattice

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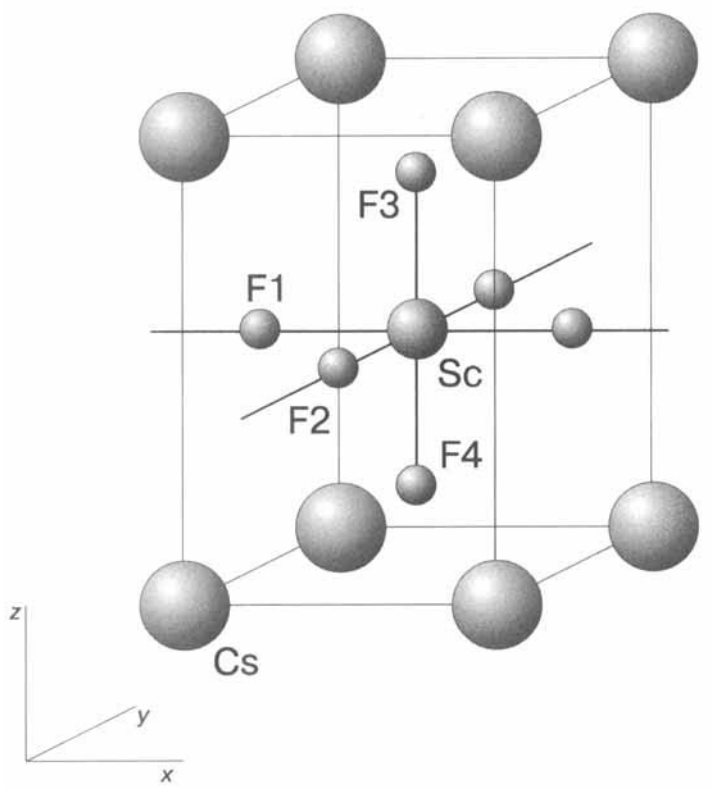

FIGURE 1 Unit cell structure of $CsScF_4$ upper tetragonal phase.

instability results in displacive phase transitions with Raman active soft modes condensation.[4, 5] To investigate such possibility for the first ($D_{4h}^1 - D_{4h}^5$) transition we've performed this work.

EXPERIMENTAL

Samples for experiments, taken from the same crystallization as in Ref. [1], were selected under polarizing microscope to avoid possible effects of crystal inhomogeneity due to ferroelastic domain structure, and cut ($1 \times 3 \times 6\,mm^3$) along crystallographic axes of D_{4h}^5 phase to obtain polarized Raman spectra. Crystals were transparent, colorless. Sample orientation was controlled during experiments by the absence of birefringence effects on incident beam. Temperature during experiment was fixed within 0.1 K.

Spectra were excited by 514 nm, 0.5 W Ar^+ polarized laser line; radiation scattered at 90° geometry was analyzed with U-1000 double grating Raman spectrometer, slit width $-2\,cm^{-1}$, scan steps $-1\,cm^{-1}$.

SYMMETRY ANALYSIS AND EXPERIMENTAL RESULTS

Vibrational representation of the D_{4h}^1 phase is

$$\Gamma = A_{1g} + E_g + 4A_{2u} + B_{2u} + 5E_u, \tag{1}$$

where only A_{1g} and E_g modes are Raman active. They correspond to vibrations of axial F atoms. For the D_{4h}^5 phase

$$\Gamma = 2A_{1g} + 2A_{2g} + B_{1g} + B_{2g} + 3E_g + 2A_{1u} + 4A_{2u} + 4A_{2u} + B_{1u} + 8E_u. \tag{2}$$

Attribution of these vibration to Raman components and structural units are given in Table I; correlations of (1) and (2) representations – in Figure 2.

It's clearly seen from Figure 1 that phase transition under investigation should result in some lines disappearance under heating the crystal above transition point, mainly due to the Brillouin zone reconstruction so, that some of them appear the zone boundary (M point).

Overview of experimental spectra at 323 K is shown in Figure 3. Frequencies of the lines observed and their attribution are summarized in Table II.

Besides listed in Table II, there are two lines: $152\,cm^{-1}$ and $255\,cm^{-1}$ in *xx*, *yy*, *zz* components, that we attributed to leaks of stronger lines from *yz* and *xy* components, respectively. Such leaks seem to be due to domain, or block, structure of our sample. Their values change from sample to sample, but we've failed to avoid them completely.

The line at $188\,cm^{-1}$ is smaller than these leaks and just a little above noise level. That is why we've marked it with (?) in Table II. In principle this

TABLE I Raman selection rules of the D_{4h}^5 phase

D_{4h}^5	*xx*, *yy*, *zz*	*xx*, *yy*	*xy*	*yz*, *xz*
F_{axial}	A_{1g}			$2E_g$
F_{planar}	A_{1g}	B_{1g}	B_{2g}	E_g

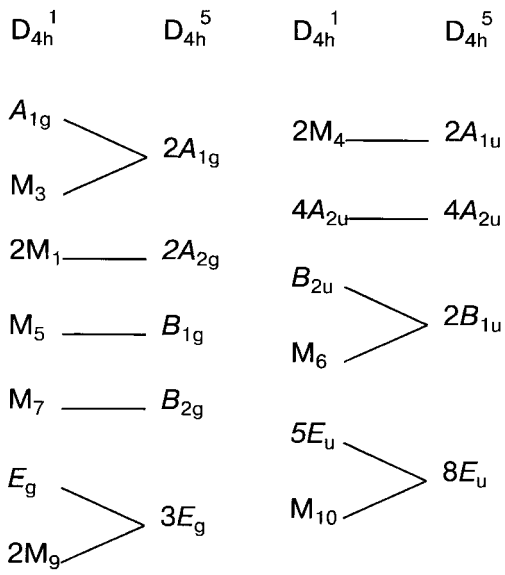

FIGURE 2 Correlations of Raman active modes for tetragonal phases of $CsScF_4$.

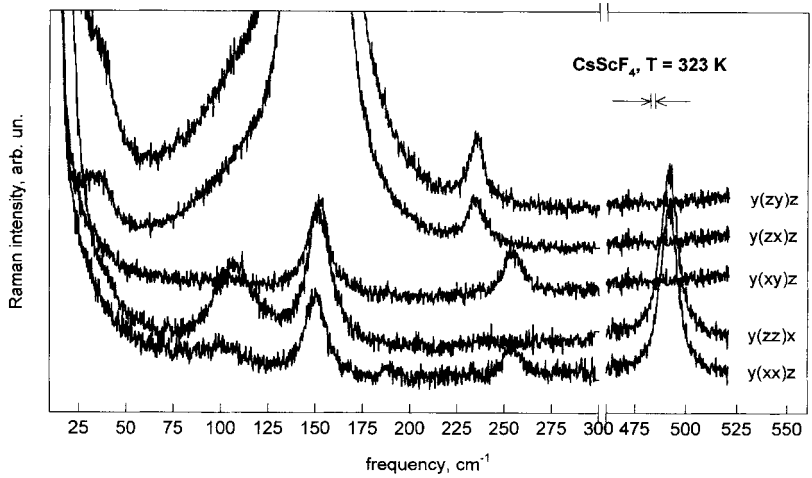

FIGURE 3 Overview of $CsScF_4$ Raman spectra. $T = 323$ K.

weak line may be due to some biphonon excitation, whereas real B_{1g} line is masked by these leaks.

Sample heating results in continuous decrease of the lines marked in Table II as medium and weak. Frequencies of the most of them change only

TABLE II Frequencies of Raman active lines and their attribution. D_{2h}^5 phase. $T = 323\,K$

Frequency, cm^{-1}	*Intensity*	*Raman component*	*Irreducible representation*
107	medium	*xx, yy, zz*	A_{1g}
495	strong		
188	weak	*xx, yy*	B_{1g} (?)
255	medium	*xy*	B_{2g}
32	medium	*yz, xz*	E_g
152	very strong		
233	medium		

slightly, according to temperature expansion of the crystal. The only exception is the line at $107\,cm^{-1}$, that goes down dramatically under temperature growth (Fig. 4; line at $152\,cm^{-1}$ is shown the as a reference). Its intensity drops continuously under heating, whereas width remains constant within experimental errors (about $1\,cm^{-1}$). Heating above phase transition point results in the disappearance of all lines except $495\,cm^{-1}$ (A_{1g}) and $152\,cm^{-1}$(E_g), that attribute them to the axial fluorine vibrations (Tab. I).

DISCUSSION

The most drastic result observed is the condensation of the full symmetry mode, shown at Figure 4. Temperature dependence of its squared frequency is given in Figure 5, and is practically linear. Wider spread of experimental points at high temperature is due to lower intensity of the line and higher noises of experimental spectra (see Fig. 4). Experimental points have been approximated (by the least squares method) to linear dependence on reduced temperature $(T - T_1)/T_1$; the best result shown at Figure 5 is obtained for $T_1 = 490\,K$, that agrees with data of previous measurements, [1] $T_1 = 475\,K$, rather well. Obtained dependence does not saturate at lower temperatures down the second phase transition at $T_2 = 317\,K$, where this frequency comes to $113\,cm^{-1}$. Such dependence is very typical for a soft mode at the phase transition of the first, close to second, order.

To investigate a mechanism driving this mode to condense, we've built a lattice dynamics model for upper tetragonal phase. Born-Mayer potential was used for sort-range interactions, and Coulomb one, in rigid ions approximation, – for the long range ones. Parameters of potentials were taken from Refs. [7, 8] and fitted to experimental frequencies of this phase and lattice equilibrium conditions (details of such simulations has been

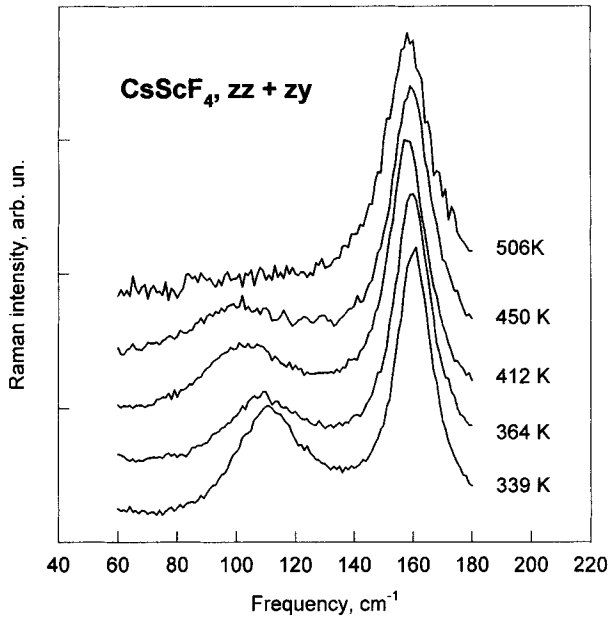

FIGURE 4 Temperature dependence of Raman active soft mode in lower tetragonal phase of $CsScF_4$.

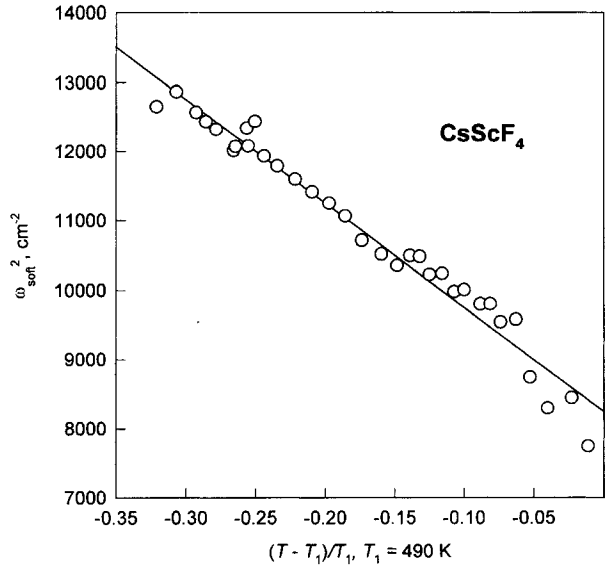

FIGURE 5 Temperature dependence of the soft mode squared frequency.

discussed earlier [9]). Phonon dispersion curves have been calculated for several typical directions of Brillouin zone; the most interesting result was obtained for the (110) one, shown in Figure 6. Here strong anticrossing of low frequency optic and acoustic modes of Σ_3 type was obtained, that results in extremely low frequency value of corresponding M_3 phonon at Brillouin zone boundary. Slight deformation of interionic potential, (for example, due to temperature expansion of lattice parameters), destroys very sensitive lattice equilibrium with respect to this lattice vibration, giving rise to lattice reconstruction. Eigenvector of this vibration is connected with antiphase rotations of rigid ScF_6 groups around z axis. Its symmetry corresponds to the irreducible representation of the soft mode, observed in Raman spectra (see Tab. II, Fig. 2).

CONCLUSION

So Raman experiments prove that tetragonal – tetragonal phase transition in $CsScF_4$ is of the first, close to the second, order, with soft mode condensation below transition temperature. This mode frequency does not saturate down the next transition into the orthorhombic phase. Distortion,

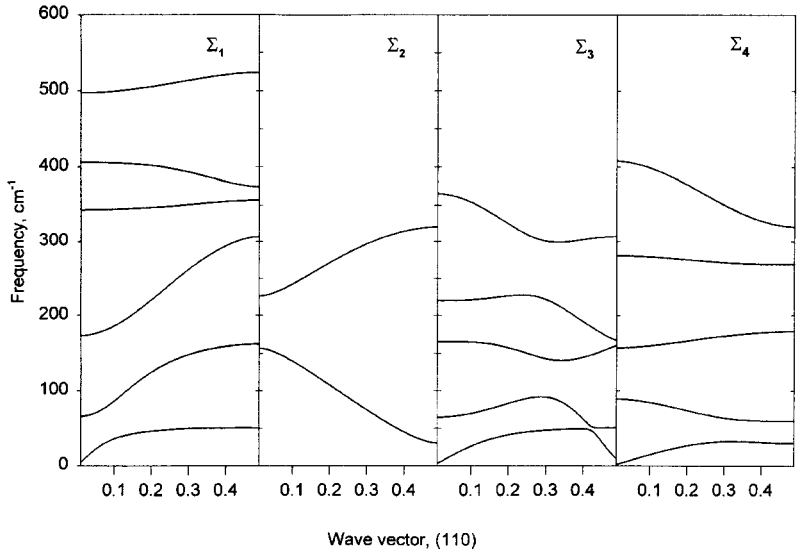

FIGURE 6 Phonon dispersion curves in upper tetragonal phase of $CsScF_4$. Mode anticrossing and nearly unstable mode at Brillouin zone boundary are seen at Σ_3 component.

that drives this transition, is antiphase rotations of rigid ScF_6 groups around z axis, induced by decompensation of long and short range interactions of structural units.

Acknowledgements

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